



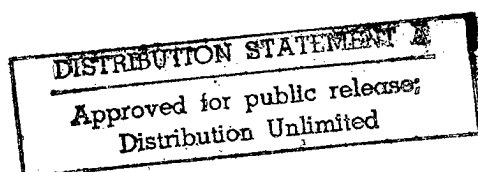
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# ***JPRS Report***

# **Science & Technology**

***Central Eurasia:  
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# Science & Technology

## CENTRAL EURASIA: Chemistry

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**An Investigation of the Catalytic Activity of Applied Catalysts Based on Nichrome and Titanium in Ozone Decomposition Reactions**

927M0140A Moscow VESTNIK MOSKOVSKOGO UNIVERSITETA: KHIMIYA in Russian Vol 33 No 2, Mar-Apr 92 (manuscript received 27 Jun 91) pp 127-131

[Article by L.I. Belskikh, L.Ye. Gorlenko, and G.I. Yemelyanova, Physical Chemistry Department; UDC 541.124.128]

[Abstract] The catalytic activity of titanium- and Nichrome-based catalysts in ozone decomposition reactions was studied. Specimens of titanium and Nichrome in the form of thin-walled cylinders were produced by a hydrodynamic pressing technique described elsewhere. Silver, iridium, and manganese dioxide were applied to the study catalysts from salt solutions and then subjected to either reduction by hydrogen at 350° (in the case of the catalysts with iridium added to them) or roasting in air at 240° (the catalysts with the silver and manganese dioxide). The ozone used in the studies was synthesized from oxygen in a laboratory-type ozone generator and was analyzed on an SF-4A spectrophotometer. The ozone decomposition reaction was studied under dynamic conditions at temperatures ranging from 20 to 200°, with an ozone concentration of 0.5 to 3% (vol), and with an ozone-oxygen mixture flow rate of 5 to 20 l/h. A Pyrex glass reactor that had been passivated in a flow of ozone-oxygen mixture was used. The reactions conducted demonstrated that applying manganese dioxide to a porous titanium surface results in an increase in catalytic activity (100% decomposition of the ozone was observed at 0°). Nichrome-based catalysts were found to display high catalytic activity at temperatures above 170°. Adding silver to them resulted in a 80° reduction in ignition temperature. The addition of iridium to titanium-based catalysts resulted in active but unstable catalysts that lost 30% of their reactivity after 30 hours. From the standpoint of activity and stability, the catalysts tested may be ranked as follows: Ag(1%)/Nichrome  $\geq$  Nichrome  $\geq$  MnO<sub>2</sub>/Ti > Ag(1%), MnO<sub>2</sub>(9.2%)/Ti > (0.6%Ir)/Ti /g titanium. Results of tests assessing the performance of the commercial granular catalyst AK-64 in ozone decomposition reactions were presented for comparison. When the same flow rates and initial concentration of ozone were used, the AK-64 and monolithic porous catalysts studied resulted in virtually the same degree of ozone decomposition. The monolithic catalysts were found to have a higher flow resistance; however, their better stability in the presence of moisture and better mechanical strength (no dust formation or entrainment of catalyst) makes them very promising for use in industrial processes. Figures 3, tables 3; references 12: 10 Russian, 2 Western.

**The Use of a Catalytic Analyzer To Measure Ozone Concentration**

927M0140B Moscow VESTNIK MOSKOVSKOGO UNIVERSITETA: KHIMIYA in Russian Vol 33 No 2, Mar-Apr 92 (manuscript received 04 Jun 91) pp 132-133

[Article by M.P. Popovich, V.I. Shishnyayev, S.N. Tkachenko, V.I. Demidyuk, V.V. Kolesnik, and V.D. Frolov, Physical Chemistry Department; UDC 542.924:546.214]

[Abstract] The literature contains several versions of an ozone analyzer based on the release of heat during the decomposition of active substances on solid surfaces. Olmer, for example, used a semiconductor thermistor coated with an ozone-decomposing catalyst as a sensor to measure ozone concentration. The authors of the study reported herein have proposed a modification of Olmer's method that makes it possible to significantly improve the sensor's operation and to measure the concentration of ozone in ozone-oxygen or ozone-air flows with a high ozone content. As the sensitive element of their ozonometer, the researchers used a thermistor that operates at elevated temperatures (up to 300°). According to their proposed technique, the thermistor is pressed into a cement-containing ozone decomposition catalyst that has an electrosipal placed inside it. A stabilized voltage is fed to the ends of the spiral. The sensor operates in an elevated temperature mode continuously, which increases its activity and stability. The catalyst-sensor's surface is restored in a very short time and may be used to make additional measurements. The heating of the catalyst and resistor may be measured by varying the voltage. In the case described, the temperature equaled 200°, and the sensor manifested a high degree of operating stability and required about 10 minutes to determine the concentration of ozone in a gas flow. The new catalyst analyzer's activity reliability was confirmed at ozone concentrations ranging from 0.01 to 8%. The results yielded by the new analyzer were determined to be reproducible within 10%. The new analysis system's sensitivity was shown to depend on flow speed and to increase as flow speed increased within the tested range from 5 to 100 l/h. Figures 2; references 2 Western.

**The Activation and Stabilization of Inorganic Catalase Reaction Biosimulators**

927M0140C Moscow VESTNIK MOSKOVSKOGO UNIVERSITETA: KHIMIYA in Russian Vol 33 No 2, Mar-Apr 92 (manuscript received 28 Dec 90) pp 134-140

[Article by T.M. Nagiyev, S.Z. Zulfugarova, and Yu.M. Shikhiyev, Institute of Theoretical Problems of Chemical Technology, Baku; UDC 577.17;66.097.6;546.215]

[Abstract] A PPF<sup>3+</sup>OH/Al<sub>2</sub>O<sub>3</sub> catalyst was synthesized. The study catalyst, a biosimulator of the catalase reaction, was prepared by the impregnation method. The carrier was roasted for 10 hours at 200° prior to preparation of the catalyst. Hemin that was obtained from the firm BDH and that contained 8.6% iron was used as the

starting preparation. The prepared catalyst specimens contained 20 mg hemin and 1 g carrier. A quantity of 0.05 g  $\text{PPFe}^{3+}\text{OH}/\text{Al}_2\text{O}_3$  catalyst was studied to establish its catalase activity. After 30 minutes at 25° in 20 ml of a 5% aqueous hydrogen peroxide solution, the catalyst (active mass, 20 mg/g) resulted in the evolution of 5.06 ml of oxygen. When 2 ml of ethyl alcohol was added to the reaction system, the amount of oxygen evolved in a 30-minute period decreased to 4.2 ml. Next, the following substances were added to the reaction system in an attempt to stabilize the catalyst: ionol, hydroquinone, orthophenylenediamine [OPDA], diphenylamine [DPA], and diphenylguanidine [DPG]. Each of these stabilizing substances was added in one of two ways: by dissolution in  $\text{H}_2\text{O}_2$  or in ethyl alcohol or else by impregnation of the catalyst with a solution of the given stabilizer. Adding hydroquinone to the reaction system reduced catalase activity from 5.05 ml to 4.0 ml when the dissolution technique was used and to 3.75 ml when the impregnation technique was used. Adding ionol (by the dissolution method) to the reaction system, on the other hand, did result in an increase in catalase activity: The amount of evolved  $\text{O}_2$  increased to 4.5 ml versus 4.2 ml  $\text{O}_2$  in systems to which an ionol stabilizer was not added. The addition of DPA to the reaction system by the impregnation technique resulted in an increase in  $\text{O}_2$  evolution to 5.3 ml. Impregnation was found to be most effective in the case of DPA, and maximum evolution occurred at a  $\text{PPFe}^{3+}\text{OH}/\text{Al}_2\text{O}_3$ :DPA ratio of 1:6. After this maximum, however, the catalyst's catalase activity dropped sharply, falling to 2.5 ml at the saturation point. OPDA, when added to the reaction system, actually had a negative effect on catalase activity. When DPG was added to the catalyst in a 1:4 ratio, evolution of  $\text{O}_2$  increased to 5.2 ml. Impregnating the catalyst with a DPG-saturated solution increased catalase activity to 5.5 ml of  $\text{O}_2$  when the impregnation technique was used. Increasing the temperature at which the  $\text{PPFe}^{3+}\text{OH}/\text{Al}_2\text{O}_3$  was roasted from 100 to 200° was found to reduce catalase activity. An entirely different picture resulted when the catalyst was rotated in an inert gas medium instead of air, however. Not only was there no loss of catalase activity as the roasting temperature was increased, but catalase activity actually increased all the way up to 600°. Catalase activity was also shown to depend on the type of carrier to which the  $\text{PPFe}^{3+}\text{OH}/\text{Al}_2\text{O}_3$  was applied. The best results were achieved when the  $\text{PPFe}^{3+}\text{OH}/\text{Al}_2\text{O}_3$  was applied to tyrosine/ $\text{Al}_2\text{O}_3$ . Figures 4, table 1; references 9: 7 Russian, 2 Western.

#### The Specifics of Catalysis by Polymer-Immobilized Complexes

927M0150A Moscow USPEKHI KHIMII in Russian  
Vol 61 No 2, Feb 92 pp 257-292

[Article by A.D. Pomogaylo, Chemical Physics Institute, Russian Academy of Sciences, Chernogolovka; UDC 541.64:66.097+661.8]

[Abstract] An attempt was made to systematize the most important factors affecting the activity and selectivity of

polymer-immobilized complexes in various catalysis processes. The review is organized into an introduction, conclusion, and sections dealing with each of the following topics: ligand exchange in metal-polymer systems; characteristic features of reactions of electron transfer in metal-polymer systems; the protective functions of a macroligand; local concentration effects in metal-polymer catalysis; problems of homogeneity and the evolution of active centers in immobilized systems; the effect that the surface density of immobilized metal complexes has on their catalytic activity; characteristic features of the effect of temperature on the catalytic properties of immobilized complexes; the contribution made by the energy of a chain's nonequilibrium configurations to catalysis; cooperative stabilization of active centers in immobilized systems; the selectivity of immobilized catalysts; and the problem of polyfunctional catalysis. The following are among the main conclusions of the review presented. The role of the macroligand is that of stabilizing the mononuclear complexes included in one-dimensional chains, two-dimensional meshes, and three-dimensional skeletons. This in turn increases the thermodynamic and kinetic stability of the system containing the macroligand. The polymer structure of a ligand enclosure impeded ligand exchange and has an impact on electron transfer reactions and redox processes. Nonvalence reactions also affect reactivity, especially the geometry of a transition state. The differences in the kinetic and activation parameters of the reactions of polymer and monomer complexes are related to conformation changes in macroligands. Economical ways of optimizing immobilized systems have been developed in theory but are only now beginning to be developed in actual practice. Catalysis by immobilized complexes is accompanied by an array of macromolecular effects, including an increased local concentration of active centers and substrate in the mass of macromolecules or in the domains close to the active centers, the effect of the spatial structure and length of the polymer chain, and the contribution of the energy of its nonequilibrium states to catalysis. In immobilized systems, evolutionary transformations of mononuclear complexes into associates occur to a lesser extent than in homogeneous systems. The methodological approaches during the design, study, and use of immobilized complexes will also likely prove very useful in the new field known as chemical biomimetics, where the processes occurring in living nature are subjected to physicochemical modeling. Figures 12, tables 9; references 107: 46 Russian, 61 Western.

#### Contemporary Approaches to the Preparation of 'Palladium-on-Carbon' Catalysts

927M0150B Moscow USPEKHI KHIMII in Russian  
Vol 61 No 2, Feb 92 pp 320-331

[Article by V.A. Semikolenov, Russian Academy of Sciences; UDC 66.097.3:661.898]

[Abstract] "Palladium-on-carbon" catalyst have attracted a good deal of attention in processes of fine

organic synthesis. Their composition is simple, i.e., metallic palladium on a carbon carrier; however, they can be produced with a broad array of properties and thus be used in a broad set of processes by varying the dispersion, particle shape, and grain distribution of the palladium or the granule size, porosity, and specific surface of the carbon. In his discussion of contemporary approaches to preparing palladium-on-carbon catalysts, the author of this review has divided his attention between the structure of carbon carriers and methods of applying palladium onto a carbon carrier. The role of the chemical nature of the surface groupings of the carbon carrier is discussed, and several techniques for modifying surface oxygen groupings (e.g., roasting the carbon carrier in an oxidizing or inert atmosphere, altering the conditions under which the carrier is treated, and selecting different oxidizing agents) are discussed. The importance of the pore structure of carbon carriers is examined along with several techniques for obtaining pores of specified sizes. The three main methods of applying palladium to a carbon carrier are discussed: applying palladium compounds in a molecularly disperse state, precipitating sparingly soluble palladium compounds, and applying palladium in the form of sols of colloidal particles. The application of palladium from colloidal solutions is said to make it possible to produce cake catalysts with an active layer about 50  $\mu\text{m}$  thick. The colloidal solution technique may be used to produce cake catalysts on carbon carriers with different microcrystalline structures and with pore volumes from 0.2 to 1.6  $\text{cm}^3/\text{g}$  or with meso- and macropores ranging from 15 to 1,000 nm and with a specific surface ranging from 10 to 1,000  $\text{m}^2/\text{g}$ . Figures 5, table 1; references 74: 26 Russian, 48 Western.

#### **X-Ray Investigation of Carriers and Applied Metal Catalysts**

927M0150C Moscow USPEKHI KHIMII in Russian  
Vol 61 No 2, Feb 92 pp 356-383

[Article by E.M. Moroz, Catalysis Institute, Siberian Department, Russian Academy of Sciences; UDC 66.097+548.734+539.26]

[Abstract] The possibilities of using a number of x-ray techniques to study multicomponent highly disperse carriers and applied metal catalysts were examined. The review is organized into an introduction, conclusion, and four sections devoted to different aspects of the topic. The section on the possibilities of x-ray methods used to study multicomponent highly disperse systems includes discussions of the method of the radial distribution of atoms, full-profile x-ray analysis, and the method of determining substructural characteristics. The next two sections cover the structural and substructural characteristics of carriers for catalysts and structural and substructural characteristics of applied and nonapplied monometallic catalysts. Special attention is paid to low- and high-temperature forms of aluminum oxides, promoted aluminum oxides, and carbon carriers. The remaining section of the review deals with the

determination of the phase composition of bimetallic catalysts. Platinum-rhenium, platinum-tin, and nickel-tin catalysts are treated separately. The information presented establishes that despite the apparent low informativity of diffraction source data (i.e., diffraction peaks are generally small and fuzzy and often superimposed upon one another), formulating experiments appropriately and using modern computer methods to process results makes it possible to obtain quite a bit of useful information regarding the phase composition and structural and substructural characteristics of carriers and applied metal catalysts when the three aforementioned x-ray methods are used. Extended x-ray absorption fine structure [EXAFS] spectroscopy, which has begun to enjoy extensive use over the past decade, has a number of advantages over the method based on atoms' radial distribution. First, EXAFS spectroscopy has a higher selectivity because independent radial distribution curves may be obtained for the local circle of each of the chemical elements in a specimen. Second, EXAFS spectroscopy makes it possible to determine not only distances between atoms and coordination numbers but also the form of atoms in the vicinity of a specified atom. The drawback of using EXAFS spectroscopy to obtain information about the phase composition of carriers and applied metal catalysts is that the information it yields concerns only one or two coordination spheres in a structure, which makes analysis of structural characteristics quite difficult. EXAFS spectroscopy yields interatomic distance values with a phase shift rather than absolute values. Despite these problems, however, EXAFS spectroscopy will likely enjoy increasing use in studies of applied metal catalysts and carriers. A combination of the EXAFS and determination of atoms' radial distribution appears to be the best approach. Figures 6, tables 7; references 129: 71 Russian, 58 Western.

#### **Tetrazolium Salts—Interface Transfer Catalysts**

927M0153A St. Petersburg ZHURNAL OBSHCHEY  
KHIMII in Russian Vol 62 (124) No 1, Jan 92  
(manuscript received 27 Sep 91) pp 3-14

[Article by G.I. Koldovskiy, A.B. Zhivich, and V.A. Ostrovskiy, St. Petersburg Technological Institute; UDC 547.796.1:542.943.7]

[Abstract] In the past decade interface catalysis has won wide-scale recognition as an effective synthesis method in organic chemistry. The main problems in obtaining suitable interface catalysts have been that many are not easily accessible, highly toxic, not stable enough at elevated temperatures, or not always possible to regenerate. A number of publications have raised hopes with regard to using quarternized nitrogen-containing heterocycles as interface transfer catalysts. The first reports of the use of tetrazolium salts as interface transfer catalysts appeared in 1985. Although all tetrazolium salts may be used in interface transfer processes, 2,3,5-trisubstituted tetrazolium salts have been shown to be best, and their composition, synthesis methods, and properties have received the most detailed treatment in the literature.

The main method of producing 2,3,5-trisubstituted tetrazolium salts is oxidation of 1,3,5-trisubstituted formazanes in their various modifications. Alkyl nitrates, lead tetraacetate, silver nitrate, chlorine, bromine, and several other reagents have been used in the formazane oxidation process, but none has yet emerged as the preferred reagent because the reproducibility of the results obtained to date has not been satisfactory. It appears that the oxidation of formazanes in the two-phase system organic solvent-water occurs in accordance with an interface catalysis mechanism and that the process is autocatalytic. The creation of a simple and effective method of producing tetrazolium salts by and large stimulated research on the use of tetrazolium salts as interface transfer catalysts in such processes as oxidation of substituted arenes, production of acyl azides and tetrazoles, and alkylation and formation of esters. Among these various applications of interface catalysis, oxidation has received particular attention in view of its importance in organic synthesis. The first successful application of interface catalysis in the oxidation of organic substrates was demonstrated by way of the example of the oxidation of olefins by potassium permanganate to carbonic acids. The technique later enjoyed extensive development in numerous research projects conducted over the course of the past decade. The oxidation of benzyl alcohol, benzaldehyde, and substituted benzaldehydes under conditions of interface catalysis has been shown to occur under very soft conditions. The situation is completely different in the case of substituted toluenes, however. Techniques have nevertheless been developed for successfully using tetrazolium salts in the oxidation of substituted toluenes and imines. The reaction of imidoyle chlorides with 5-substituted tetrazoles has proved to be yet another graphic example of the advisability of using interface catalysis. Studies of the reaction of imidoyle chlorides with 5-substituted tetrazoles under conditions of interface catalysis have demonstrated that in the presence of 2,3-diphenyl-5-butyltetrazolium bromide, not only does the anticipated 2-imidoyle tetrazole appear in the first stage of the reaction but isomeric 1-imidoyle tetrazole also appears as well. Heating isomeric imidoyle tetrazoles in the absence of a solvent or in such solvents as toluene or m-xylene results in 3H-1,3,4-benzotriazepine instead of the anticipated 3,4,5-trisubstituted 1,2,4-triazole. This and other published examples demonstrate the entirely unexpected possibilities that develop when familiar reactions are re-examined under conditions of interface catalysis. Tables 3; references 51: 29 Russian, 22 Western.

**Tetrazoles. XXIX. The Imidoylation of 5-Aryl Tetrazoles Under Interface Catalysis Conditions; The Formation of 3H-1,3,4-Benzotriazepines**

927M0153D St. Petersburg ZHURNAL OBSHCHEY KHIMII in Russian Vol 62 (124) No 1, Jan 92 (manuscript received 27 May 91) pp 194-198

[Article by G.I. Koldovskiy, I.V. Nikonova, A.B. Shvich, V.A. Ostrovskiy, and V.S. Poplavskiy, St. Petersburg Technological Institute; UDC 547.796.1:542.943.7]

[Abstract] In an effort to better understand the mechanism of the reaction of tetrazoles with electrophilic reagents, the authors studied the reaction of 5-aryl tetrazoles with N-arylbenzimidoyl chlorides under conditions of interface catalysis. Next, they studied the thermolysis of imidoyle tetrazoles formed during that reaction. The imidoylation of the 5-aryl tetrazoles was conducted in the two-phase system methylene chloride-water at 20°C. Either tetrabutyl ammonium bromide (I) or 2,3-diphenyl-5-butyl tetrazolium bromide (II) served as the catalyst in the individual reactions. Under the study conditions, the respective imidoyle tetrazoles were formed in an 85-90% yield. Attempts to isolate individual imidoyle tetrazoles proved unsuccessful due to their poor heat stability, however. The <sup>13</sup>C NMR spectra of the products formed during the reaction of 5-aryl tetrazoles with N-arylbenzimidoyl chloride contained four signals at  $\delta = 150.42, 154.36, 163.87, \text{ and } 164.22$  ppm, thus confirming the presence of two isomers, namely, 1-imidoyle- and 2-imidoyle-5-phenyl tetrazole, in the reaction mixture. Further analysis of the <sup>13</sup>C NMR spectra revealed that the 1-imidoyle- and 2-imidoyle-5-phenyl tetrazole were present in the form of Z- and E-isomers, which is to say that the reaction of 5-aryl tetrazoles with N-arylbenzimidoyl chloride is non-stereo-specific. In the second stage of their studies, the authors examined the thermolysis of isomeric 1-imidoyle- and 2-imidoyle-5-aryl tetrazoles. When the two compounds were heated to 85-120°C in the absence of a solvent or in solvents such as toluene, m-xylene, or dioxane, 3H-1,3,4-benzotriazepines formed instead of the expected 3,4,5-trisubstituted 1,2,4-triazoles. The transformation of 1-imidoyle-5-aryltetrazole into triazepine was shown to pass through a stage of isomerization into 2-imidoyle-5-aryltetrazole, as was recently confirmed elsewhere by indirect methods. The authors concluded by stating that the thermolysis of 1-imidoyle- and 2-imidoyle-5-aryl tetrazoles is a convenient method of synthesizing 1,3,4-triazepines that are not substituted at their nitrogen atoms. Tables 2; references 16: 7 Russian, 9 Western.

**The Most Likely Mechanism of the Catalytic Hydration of Nitriles**

927M0154A Alma-Ata IZVESTIYA AKADEMII NAUK RESPUBLIKI KAZAKHSTAN: SERIYA KHIMICHESKAYA in Russian No 3 (273), May-Jun 92 (manuscript received 3 Jun 92) pp 42-46

[Article by K.A. Ayapergenov and M.G. Finayeva, Organic Synthesis and Coal Chemistry Institute, Republic of Kazakhstan Academy of Sciences, Karaganda; UDC 541.124]

[Abstract] The authors of the study reported herein have examined what they believe is the most likely mechanism of the catalytic hydration of 4-cyanopyridine in the presence of the anion-exchange resin AV-17-8 at a specified temperature. A comparison of the reaction of the hydration of 4-cyanopyridine with and without the AV-17-8 catalyst revealed that without a catalyst present, the

molecules of the starting substances have low dipolar moments. With an AV-17-8 catalyst present, on the other hand, they are strongly polarized, and their dipole moments change to the extent that the reaction appears to be occurring in accordance with an entirely different mechanism. The course of the reaction is easier, and its activation barrier is lowered significantly. In the reaction space, the water molecules form associates that have a one-dimensional (linear) and multidimensional structure. The water molecules located in the central part of these complexes are less active than their peripheral counterparts or perhaps even inactive. This does not, however, preclude the possibility that the water molecules located in the center portion of the linear and three-dimensional chains of the complex will participate in the reaction. The formation of a complex between the molecules of the reagents and the catalyst is also likely. The coordination number of a hydroxide ion is 3; consequently, the OH may be coordinated with two water molecules. Because of this fact, the free nitrile molecule tends to draw closer to the OH ion. As the nitrile approaches the anionite, the interaction of electrostatic fields in the interacting molecules is accompanied by a shift of the electron density from the positive charged part to the negative end of the dipole. This necessitates completion of the work on which the energy of the nitrile's forward motion is expended. In the general case, complete interaction of the two dipoles results from the rotational motion. In the particular case under consideration, their direct interaction may result. In any case, the energy stored by the forward and rotational degrees of freedom is expended on further polarization of the bond. The reaction of the water with the polarized nitrile results in formation of the end product. The authors state that, in their view, the occurrence of the two steps described, i.e., adsorption of the nitrile and complexing of the water to it, corresponds to the easily solvable problem of the encounter of two particles. They acknowledge that others have explained the reaction under consideration in terms of the synchronous reaction of reagents on the catalyst surface (termed the concert mechanism). The authors conclude by saying that while this hypothetical mechanism cannot be discarded, the actual ordered encounter of four or five particles seems unlikely. References 8: 6 Russian, 2 Western.

#### The Dehydration of Propyl Alcohol in the Presence of a Borophosphate Catalyst

927M0154B Alma-Ata IZVESTIYA AKADEMII NAUK RESPUBLIKI KAZAKHSTAN: SERIYA KHIMICHESKAYA in Russian No 3 (273), May-Jun 92 (manuscript received 12 Jul 91) pp 47-52

[Article by Zh.B. Kurmanova, G. Bayyesheva, M. Salykbayeva, M.M. Kursina, Yu.A. Moiseyev, and N.R. Bukeykhanov, Institute for the Chemistry of Oil and Natural Salts, Republic of Kazakhstan Academy of Sciences, Guryev; UDC 517.315.25.057:547.28:542.936]

[Abstract] The dehydration of propyl alcohol in the presence of a borophosphate catalyst was examined.  $BPO_4$  was prepared as described elsewhere, homogenized with CaO and ZnO, and pressed into tablet form by a manual press under a pressure of 100 to 200 kg/cm<sup>2</sup>. The tablets were then roasted in air for 3 hours at 600°C. The process of the dehydration of chemically pure propyl alcohol was studied in a pulsed mode on a microcatalytic unit with a Tsvet chromatograph. Hydrogen fed in at a rate of 30 ml/min served as the carrier gas. Between 80 and 100 mg of catalyst with a grain size of 0.15 to 0.3 mm was used. A DRON-2 was used to perform x-ray phase analyses of the catalysts, and mercury porometry was used to determine pore size distributions, specific volume, and surface. Pure  $BPO_4$  resulted in a conversion factor of 99.38 at a temperature of 420°C. In the case of the system  $BPO_4$ /CaO, the same degree of conversion was reached at 330°C. The system containing 5% (mass) ZnO was found to occupy an intermediate position. Besides resulting in an increased degree of conversion at a reduced temperature, the addition of 5% (mass) CaO offered the additional benefit of good mechanical strength. Pure borophosphate catalyst was found to have a mechanical strength of 80 kgf/cm<sup>2</sup> and to lose between 40 and 50% of its mass to hydration and entrainment by the flow. The catalyst consisting of  $BPO_4$  plus 5% CaO had a mechanical strength of 188 kgf/cm<sup>2</sup>.  $BPO_4$  with 10% CaO added to it, on the other hand, had a mechanical strength index of only 130 kgf/cm<sup>2</sup>. Further studies established that a concentration of 5% (mass) CaO was optimum in that it provided the best combination of mechanical strength and activity. Figures 4, table 1; references 4: 3 Russian, 1 Western.

#### The Composition of Products of the Dehydrochlorination of 3-(β-Chloroethyl)benzoxazolinone Under Interface Catalysis Conditions

927M0158B Tashkent UZBEKSKIY KHIMICHESKIY ZHURNAL in Russian No 6, Nov-Dec 91 (manuscript received 21 Nov 90) pp 36-38

[Article by T.Yu. Bukhareva and N.A. Aliyev, Red Labor Banner Order Plant Chemistry Institute, Republic of Uzbekistan Academy of Sciences; UDC 547.787.3]

[Abstract] The transformation of 3-(β-chloroethyl)benzoxazolinone under conditions of interface catalysis was studied. In an earlier study, the authors demonstrated that eliminating hydrogen chloride from 3-(β-chloroethyl)benzoxazolinone under conditions of interface catalysis results in a complex mixture of products. The main product constituting this mixture was determined to be N-vinylbenzoxazolinone ( $R_f$  0.95; melting point, 48-50°C). Studies performed in a continuation of this previously reported research established that dehydrochlorination of 3-(β-chloroethyl)benzoxazolinone under conditions of interface catalysis results in the formation of small quantities of O-(β-oxyethyl)benzoxazole (a brown liquid with an  $R_f$  value of 0.16) and N-(β-ethoxyethyl)-benzoxazolinone (a

transparent liquid with an  $R_f$  value of 0.47) in addition to the expected N-vinylbenzoxazolinone ( $R_f$  0.95). The dehydrochlorination of 3-( $\beta$ -chloroethyl)benzoxazolinone was performed as follows. Next, 40 ml ether and 25 ml dioxane were added to  $\beta$ -chloroethylbenzoxazolinone (7.88 g, i.e., 0.04 mole). Next, 0.6 g (0.0026 mole) triethylbenzylammonium chloride and 9 ml of a 50% aqueous solution of KOH were added. The reaction was conducted under intense stirring at a temperature of 35°C for 10 hours. The reaction mixture was then filtered, and the solvent was removed. Column chromatography was used to separate N-vinylbenzoxazolinone (in a 15% yield), O-( $\beta$ -oxyethyl)-benzoxazole (in a 3% yield), and N-( $\beta$ -ethoxyethyl) benzoxazolinone (in a 5% yield). References 7: 6 Russian, 1 Western.

#### Study of Ni-Pd Catalyst Surfaces by IR-Spectroscopy

927M0166A Moscow IZVESTIYA AKADEMII NAUK SERIYA KHIMICHESKAYA in Russian No 6, Jun 92 (manuscript received 4 Aug 91) pp 1276-1281

[Article by A. A. Vedenyapin, S. V. Yushin, L. T. Kondratyev, and A. L. Lapidus, Organic Chemistry Institute imeni N. D. Zelinskiy, Moscow; UDC 541.128:541.183.26:543.422.8]

[Abstract] Bi-metallic Ni-Pd catalysts on alumina carrier exhibit properties and adsorption characteristics notably different from those of Ni-on-alumina or Pd-on-alumina according to qualitative IR-spectroscopic data. In the present work IR spectroscopy was used in conjunction with volumetric adsorption technique to make a quantitative study of the interaction of carbon monoxide with the surfaces of Ni, Pd, and Ni-Pd catalysts carried on  $\gamma$ -alumina at 25°C. Quantitative IR data are presented for five absorption bands. Figures 2; references 13: 7 Russian, 6 Western.

#### Study of Catalytic Activity of Metal Complexes Fixed on Solid Carrier. Report 10. Selective Hydrogenation of Allyl Benzene in Presence of Heterogeneous Pt-Sn-Citrate Complexes

927M0166B Moscow IZVESTIYA AKADEMII NAUK SERIYA KHIMICHESKAYA in Russian No 6, Jun 92 (manuscript received 29 Apr 91) pp 1287-1290

[Article by L. I. Gvinter, N. V. Dyakonova, T. P. Lutsko, V. Z. Sharf, and P. G. Antonov, Organic Chemistry Institute imeni N. D. Zelinskiy, Moscow; St. Petersburg Technological Institute; UDC 541.49:541.128:542.941.7:547:313.6]

[Abstract] Complexes of platinum with Sn(II) halides are well known as catalysts for hydrogenation and isomerization of unsaturated hydrocarbons. The catalytic properties of platinum-tin complexes result from their capability to activate hydrogen due to the high trans-effect of tin-containing ligands. Also, the nature of the substituent at the tin atom has a great effect on the properties of

these complexes. In the present work the catalytic properties of platinum-tin-citrate complexes, fixed on a carrier to increase stability, were studied for the first time. The new heterogeneous catalysts manifested a high selectivity in hydrogenating allyl benzene into propyl benzene without accelerating isomerization of the carbonyl double bond. The activity of the complexes depends on their functional conditions and decreases as the Sn:Pt ratio is raised. Figure 1; references 6: 4 Russian, 2 Western.

#### Metal Complexes in Catalytic Conversions of Olefins. Report 5. Catalytic Synthesis of $C_{19}$ - $C_{24}$ Olefins from Propylene

927M0166D Moscow IZVESTIYA AKADEMII NAUK SERIYA KHIMICHESKAYA in Russian No 6, Jun 92 (manuscript received 17 Apr 91) pp 1299-1303

[Article by D. B. Furman, A. O. Ivanov, A. Yu. Belyankin, A. G. Pogorelov, T. V. Yanchevskaya, and O. V. Bragin (deceased), Organic Chemistry Institute imeni N. D. Zelinskiy, Moscow; UDC 547.512:547.4]

[Abstract] Previously, a catalytic system was presented based on zero-valence triphenylphosphine complex  $Ni(PPh_3)_n$  ( $n = 2-4$ ) combined with sesquichloroethyl aluminum (SCEA) for the dimerization of liquid propylene. The system manifested high activity (35-48 kmol propylene per mole of Ni) and dimer selectivity (85-96 percent). The remaining products consisted of propylene oligomers containing from three to eight links. These olefins are used as high octane number motor fuel additives and as components for the synthesis of non-ionogenic surfactants. In the present work optimum conditions were found for obtaining  $C_{19}$ - $C_{24}$  olefins by oligomerization of liquid propylene in the presence of the above catalytic system. It was demonstrated that the resulting hexenes are subject to secondary di- and trimerization reactions. Figure 1; references 3 (Russian).

#### Electrochemically Induced Processes for Formation of Phosphorus Acid Derivatives. Report 2. Role of Polymerization Processes in Electrosynthesis of Phosphorus Acids Esters from White Phosphorus

927M0166F Moscow IZVESTIYA AKADEMII NAUK SERIYA KHIMICHESKAYA in Russian No 6, Jun 92 (manuscript received 6 Jun 91) pp 1328-1333

[Article by A. S. Romakhin, I. M. Zaripov, Yu. Budnikova, Yu. M. Kargin, Ye. V. Nikitin, A. P. Tomilov, and Yu. A. Ignatyev, Organic and Physical Chemistry Institute imeni A. Ye. Arbuzov, Kazan; Kazan State University imeni V. I. Ulyanov-Lenin; UDC 541.138.(546.18+547.1'118)]

[Abstract] While studying the mechanism of electrosynthesis of phosphorus acid esters from white phosphorus in the preceding work, for simplicity's sake the phosphorus polymerization stage was overlooked, although it

is well known that this stage is an insurmountable blockage in the synthesis of organophosphorus compounds. Much accumulated experimental material indicates that the polymerization stage is complex and depends much on the synthesis conditions. The conversion of white phosphorus into end products is a heterogeneous process due to the low solubility of  $P_4$  and its oligomeric forms in the studied reaction media, so that the phosphorus exists in a separate phase. A nucleophilic reagent thus reacts with white phosphorus on the surface of a phosphorus droplet, which in its turn favors polymerization. Also, it is not possible to exclude the probability of the phosphide anion reacting in various directions such as formation of three-dimensional "grafted"

structures which are much less reactive in further transformations under more severe conditions. In the present work a study was made of the mechanism of electrosynthesis of phosphorus acid esters from white phosphorus and it was demonstrated that the reaction flows in two directions - monomeric, with dissolved phosphorus, and polymeric, with the phosphorus occurring on the surfaces of emulsified droplets. In alcoholic solution, most of the end product is formed from an intermediate polymer. Study of the dynamics of accumulation of products in solution during the electrolysis will facilitate study of the mechanism of phosphorus reaction at other stages of the process. Figure 1; references 7: 1 Russian, 6 Western.

**Kinetic Laws Governing the Oxidation of 2,4-Dichlorotoluene**

927M0157A Tashkent *UZBEKSKIY KHIMICHESKIY ZHURNAL* in Russian No 5, Sep-Oct 91 (manuscript received 16 Jan 91) pp 8-11

[Article by U.T. Usmankhodzhayev, S.S. Khamidov, U.M. Azizov, and S.I. Iskandarov, All-Union Chemical Technology Scientific Research Institute of the Medical and Microbiological Industry; UDC 547.539:543.943.7]

[Abstract] The kinetic laws governing the oxidation of 2,4-dichlorotoluene by the oxygen of air in a medium of ice-cold acetic acid in the presence of a cobalt-manganese-bromide system were studied. Preliminary studies established that the study reaction occurs in the kinetic range at temperatures between 100 and 180°C when a pressure of 14 atm and an air feed rate of more than 100 l/h are used. For this reason, oxidation of the 2,4-dichlorotoluene was conducted under a pressure of 16 atm with an air feed rate of about 150 l/h per mole of 2,4-dichlorotoluene and with 2,4-dichlorotoluene concentrations of 0.3 and 1.0 mol/l. As the temperature was increased from 100 to 160°C, the initial rate of 2,4-dichlorotoluene oxidation increased by more than a

factor of 3. The initial oxidation rate was found to be virtually independent of the concentration of 2,4-dichlorotoluene in the starting mixture. Adding small amounts of manganese salts ( $8.5 \times 10^{-4}$  mol/l) to the study cobalt catalyst (consisting of  $1.0 \times 10^{-2}$  mol  $\text{Co}^{+2}$ /l and  $6.0 \times 10^{-2}$  mol  $\text{Br}^-$ /l) was found to help increase the initial oxidation rate from 2.68 to  $4.4 \text{ mol/l} \times \text{min} \times 10^2$ . This increase in oxidation rate was attributed to a synergetic effect that in turn resulted in an acceleration of the reduction of the active trivalent form  $\text{Co}^{+3}$  and an increase in the concentration of primary radicals. The total concentration of catalyst also affected the oxidation rate of 2,4-dichlorotoluene. After a certain amount of time, however, the oxidation reaction came to a virtual halt. The authors hypothesized that this cessation of oxidation was due to the fact that substances inhibiting the reaction process accumulated in the reaction products by the stage of oxidation of 2,4-dichlorotoluene to 2,4-dichlorobenzaldehyde. This hypothesis was confirmed by data regarding the Co (II)-Co (III) valence transformation and the changes in the concentration of  $\text{Br}^-$  and 2,4-dichlorobenzaldehyde during the process of the oxidation of 2,4-dichlorotoluene. Figures 3; references 1 (Russian).

**Electrochemistry of Autocomplex-Type Compounds. 1. An Electrochemical Investigation of Autocomplexes of the Picryl Series**

927M0153C St. Petersburg ZHURNAL OBSHCHEY  
KHIMII in Russian Vol 62 (124) No 1, Jan 92  
(manuscript received 3 Jul 90) pp 188-193

[Article by K.P. Butin, I.G. Ilina, A.A. Moiseyeva, and  
O.A. Reutov, Moscow State University imeni M.V.  
Lomonosov; UDC 547.546+541.138]

[Abstract] The term "autocomplex" refers to compounds with intramolecular charge transfer in which charge transfer may occur either by direct polar conjugation between donor and acceptor fragments of the molecular along the chain of bonds through a nitrogen bridge atom or else through donor-acceptor interaction of functional groups through space (this is also referred to as "contact transfer"). According to the main criterion for classifying compounds as autocomplexes, their electron spectra must manifest a linear dependence between the position of the maximum of the long-wave band and the model ionization potential of the corresponding donor fragment. No distinct linear dependence is observed in the case of picryl derivatives, however, and in a number of cases, its long-wave maximum is complex. Quantum chemical calculations of the electron spectra of these compounds have established that direct polar conjugation is the main contributor to the long-wave band and that the contribution of "contact transfer" does not exceed 10%. In an effort to determine whether it is possible to make an independent estimate of the contribution of a "contact transfer" charge in autocomplexes of the picryl series, the authors of the study reported herein conducted an electrochemical study of compounds of the picryl series. Specifically, they compared the electrochemical redox-potentials of autocomplexes of the picryl series with the redox-potentials of their respective 2,4-dinitrophenyl, 2-nitrophenyl, and 4-nitrophenyl analogues as well as with those of corresponding individually selected donor amines. The study compounds were all synthesized as reported elsewhere. All of the electrochemical measurements were made in anhydrous acetonitrile against a background of 0.05 M  $\text{Bu}_4\text{NBF}_4$  on a rotating or platinum electrode. The oxidation potentials of compounds of the trinitrophenyl and dinitrophenyl series containing one and the same donor fragment were compared. On the basis of this comparison, the authors proposed the following formula for use in estimating the percentage of the "contact contribution" [K] to total charge transfer in picryl derivatives:  $K = (E_{\text{I}}^{\text{Ox}} - E_{\text{II}}^{\text{Ox}}) / (E_{\text{I}}^{\text{Ox}} - E_{\text{V}}^{\text{Ox}}) \times 100\%$ . According to calculations made with this formula, the contribution of the "contact transfer" charge does not exceed 10%. Tables 2; references 14: 10 Russian, 4 Western.

**Electrochemical Regeneration of Tetravalent Cerium**

927M0158A Tashkent UZBEKSKIY KHIMICHESKIY  
ZHURNAL in Russian No 6, Nov-Dec 91 (manuscript  
received 3 Apr 91) pp 9-11

[Article by L.I. Leontyeva, U.M. Azizov, and R.M. Ilina,  
All-Union Scientific Research and Chemical Technology  
Institute of the Medical and Microbiology Industry;  
UDC 546.42;547.82;543.25]

[Abstract] The authors of the study reported herein have developed and proposed an electrochemical method of regenerating Ce (IV) ions from spent sulfuric acid solutions and a spectrophotometric method for quantitative determination of Ce (IV) from sulfuric acid solutions containing a large amount of  $\text{Ce}^{+4}$ . The new method is based on the use of inexpensive and readily available electrodes, specifically, a stainless steel (12Cr18Ni10Ti) cathode and graphite anode. The electrolysis is performed in a glass vessel with a capacity of 200 ml. The anion exchanger and cation exchanger are separated by a porous enclosure. The electrolyzer is filled with a solution of sulfuric acid Ce (III) salts in a concentration of 80 g/l in a mixture of 10% sulfuric and nitric acids in 10:1 ratio. The temperature is kept stable at 70°C. A direct current with a strength of 2 A is passed through the said system for 40 minutes. A 90-95% yield of regenerated sodium (IV) sulfate may be achieved by using the new technique. The product yield was found to depend not only on the shape and dimensions of the electrodes but also on their location relative to one another. The best results were achieved when plate electrodes were configured parallel to one another at a distance of 4 cm from one another. The method developed for quantitative determination of Ce (IV) is based on the ability of sulfuric acid Ce (IV) to turn a solution bright orange (as opposed to Ce (III), which remains colorless). References 6: 3 Russian; 3 Western.

**The Electrochemistry of Transition Metal Monocrystals With Well-Tested Surfaces**

927M0161A Moscow USPEKHI KHIMII in Russian  
Vol 61 No 4, Apr 92 (manuscript received ) pp 734-764

[Article by G.V. Khaldeyev and T.A. Syur, Perm State  
University imeni A.M. Gorkiy; UDC 541.138]

[Abstract] Data obtained in the past few years regarding the effect that the reconstruction of the first surface layers due to the adsorption-chemical effect of electrolyte particles has on the conditions of the formation of a new phase during the electrochemical process was analyzed. Along with an introduction and conclusion, the review contains sections devoted to the following topics: surface defects and a model of the discrete lattice of a metal; the orientation dependence of the dissolution of metal during phase transitions of the first type (corrosion, electrocrystallization); adsorption of chalcophilic particles and phase transitions of the second type in the

near-surface layers of monocrystals (the term "transitions of the second type" refers to changes that are not true phase transitions in the conventional sense but that change the close order of hierarchical structures in binary electrical layers of both the electrolyte and metal); and reconstruction of the monocrystals' surfaces upon the adsorption of hydrogen, oxygen, and halides. Special attention is paid to the adsorption of hydrogen by copper, ruthenium, rhodium, tungsten, and platinum and to the adsorption of halides by platinum, silver, gold, and copper. The reviewers conclude that analysis of the metastable states of the near-surface layer of metal crystals under conditions of contact with a condensed (electrolyte) and noncondensed (gas) medium has made it possible to set forth new approaches to electrochemical-corrosion processes, i.e., to phase transitions of the first type, that are accompanied by the evolution of gases on the surface and by the adsorption and implantation of light chalcophilic particles. The system hydrogen-saturated metal-electrolyte has been shown to possess unique features: The hydrogen in the metal, which has an anomalously high diffusion factor, is easily redistributed in the lattice and interacts with surface and subsurface defects so as to change their concentration, topology, and energy state. Another outstanding feature of the behavior of hydrogen in condensed media is its ease of losing or acquiring an electron, which in turn makes the following possible: synthesis of heavier particles from hydrogen protons dissolved in metal, the participation of  $H^-$  and  $H^+$  in acts of the deprotonation of adsorbed aqueous structures, and the formation of new compounds in adsorbed films. The electrochemistry of monocrystals with well-tested surfaces is hailed as a promising new direction in electrochemistry that will make it possible to analyze surface restructuring by means of a set of high-resolution physical methods and that will not only create a qualitatively new level of knowledge regarding such surfaces but that will also compel a reassessment of conventional electrochemical approaches based solely on an analysis of integral kinetic information regarding the transfer of charges through a metal-electrolyte interface. Figures 19, tables 4; references 94: 20 Russian, 74 Western.

#### **Inhibition-Initiation During the Pyrolysis of Hydrocarbons**

927M0161B Moscow USPEKHI KHIMII in Russian  
Vol 61 No 4, Apr 92 pp 792-814

[Article by L.V. Shevelkova, L.Ye. Guselnikov, G. Bach, and G. Zimmermann, Petrochemical Synthesis Institute imeni A.V. Topchiyev, Russian Academy of Sciences, Moscow, and Central Organic Chemistry Institute, Leipzig, Germany]

[Abstract] The results of research on the processes of the thermal decomposition of hydrogens and the formulation of a general concept of the mechanism of their mutual effect were examined. The reviewers concentrate most of their attention on the pyrolysis of binary mixtures of hydrogens that are either crude materials used in

commercial pyrolysis processes or else by-products thereof. Separate sections of the review are devoted to the pyrolysis of mixtures of alkanes and alkenes, alkanes and dienes, mixtures of alkanes, mixtures of alkanes and cycloalkanes, the effect of aromatic hydrocarbons, and the mechanism of inhibition-initiation during the pyrolysis of hydrocarbon mixtures. On the basis of the material presented, the reviewers formulate a general concept of the inhibition-initiation mechanism at play during the pyrolysis of mixtures of different-class hydrocarbons. According to the proposed mechanism, binary mixtures of hydrocarbons involved in a pyrolysis process may be viewed in terms of a system of reactions among different types of radicals competing to continue the chain. Accordingly, one and the same hydrocarbon in a copyrolysis process may function as either an inhibitor or an initiator of decomposition depending on the nature of its partner's behavior and the present concentration of active radicals: the hydrocarbon functioning as the inhibitor has a lower concentration of radicals leading the chain than its partner has at the given moment. This proposed mechanism is said to explain the effectiveness and direction of the effect of one hydrocarbon on the decomposition of another as a function of its chemical structure and process conditions and to also explain the nonadditivity of the formation of products during the pyrolysis process. This is shown to be especially true in the case of the nonadditivity of the products formed during the pyrolysis of alkanes with propylene and isobutylene additives. A two-page table detailing the mutual effect that  $C_2$  through  $C_9$  alkanes have on the decomposition rate during the pyrolysis of binary mixtures thereof is included. Figures 8, tables 3; references 90: 47 Russian, 43 Western.

#### **Electrochemically Induced Processes for Formation of Phosphorus Acid Derivatives. Report 1. Synthesis of Trialkyl Phosphates from White Phosphorus**

927M0166E Moscow IZVESTIYA AKADEMII NAUK  
SERIYA KHIMICHESKAYA in Russian No 6, Jun 92  
(manuscript received 6 Jun 91) pp 1322-1327

[Article by A. S. Romakhin, Yu. G. Budnikova, I. M. Zaripov, Yu. M. Kargin, Ye. V. Nikitin, A. P. Tomilov, Yu. A. Iznatyev, and V. V. Smirnov, Organic and Physical Chemistry Institute imeni A. Ye. Arbuzov, Kazan; Kazan State University imen V. I. Ulyanov-Lenin; UDC541.138:(546.18+547.1'118)]

[Abstract] The problem of direct implementation of white phosphorus has become more pressing as a result of the vigorous development of organophosphorus chemistry and the ecological problems associated with large scale industrial production of these compounds. Experimental material collected thus far on the synthesis of these compounds was obtained mostly under severe thermal conditions and for very complex multi-component systems where it is difficult to determine even an approximation of the mechanism of the process. Most progress has been made on synthesis methods

based on the joint action of nucleophilic and electrophilic reagents on white phosphorus. The P atom in the  $P_4$  tetrahedron manifests very weak nucleophilic properties; however, as a result of ring stress and weakness of the P-P bond, the P atoms, as weak electrophiles, react readily with various nucleophiles. The resulting phosphide anion, as a weak base and nucleophile, may become stabilized by reacting with various electrophilic components in the solution, e.g. alkyl halide, protons, aldehydes, etc. Repetition of the nucleophile attack stage and subsequent capture of the phosphide anion by an electrophilic reagent makes it possible to obtain a variety of products under mild conditions. It thus appeared expedient to utilize these theoretical considerations to design electrochemical reactions utilizing white phosphorus. In the present work a study was made of the conditions for sequential rupture of P-P bonds in the  $P_4$  molecule, oligomerization and state of electrochemically generated nucleophilic components, rules governing subsequent electrochemical and chemical reactions of primary intermediates with various nucleophiles (alcoholate-, hydroxide-, phenolate-ions) and anode generated electrophiles and other elementary acts in the overall process of organophosphorus compound synthesis from white phosphorus. It was demonstrated that alcoholate ions react with white phosphorus in alcoholic solutions in the presence of anode-generated iodine to form phosphoric acid esters. A process mechanism is proposed wherein the intermediate products consist of dialkyl and trialkyl phosphites with dialkylalalkyl phosphonates as side products. References 14: 3 Russian, 11 Western.

**Electrochemical Reduction Destruction of Polyethylene Terephthalate Under Galvanostatic Conditions. The Effect of the Nature of an Indifferent Electrolyte**

927M0169B Moscow ELEKTROKHIMIYA in Russian  
Vol 28 No 6, Jun 92 (manuscript received 11 Dec 90)  
pp 880-886

[Article by A.A. Pud, G.S. Shapoval, A.P. Tomilov, and O.E. Mikulina, Bioorganic Chemistry and Petrochemistry Institute, Ukraine Academy of Sciences, Kiev; UDC 541.138.3:547.322]

[Abstract] The electrochemical reduction destruction of polyethylene terephthalate under galvanostatic conditions and in the presence of different tetraalkyl ammonium salts was examined. The primary objective was to determine the effect that the conditions of galvanostatic electrolysis and the nature of an indifferent electrolyte have on the electrochemical destruction of polyethylene terephthalate. A new thin-layer cell was used to study the electrochemical reactions and subsequent transformations of the solid-phase study polymers. The new cell made it possible to create a rather high and reproducible three-phase interface. For the experiments, the researchers used polyethylene terephthalate films 50  $\mu\text{m}$  thick with an area of  $1.5 \times 4 \text{ cm}^2$ . All of the experiments were performed in a 0.1 M solution of various tetraalkylammonium salts in dimethylformamide. The following electrolyte compositions were studied:  $(C_4H_9)_4NI$ ,  $(C_4H_9)_4NBr$ ,  $(C_4H_9)_4NBF_4$ ,  $(C_4H_9)_4NClO_4$ ,  $(C_2H_5)_4NClO_4$ , and  $(CH_3)_4NClO_4$ . The studies performed established that for current densities less than  $1.9 \text{ mA/cm}^2$ , the efficiency of the electrochemical reduction destruction of polyethylene terephthalate is linearly dependent on the amount of electricity passed through the system. At higher current densities, the efficiency of electrochemical reduction destruction decreases because a portion of the electricity is expended to reduce the components of the background solution. The studies further demonstrated that the  $E_{1/2}$  of polyethylene terephthalate depends on the nature of the anion and on the size of the electrolyte's tetraalkylammonium cation. The values obtained for the  $E_{1/2}$  of the polyethylene terephthalate waves became more positive upon a switch from the  $(C_4H_9)_4N^+$  electrolyte to the  $(CH_3)_4N^+$  electrolyte. The electrochemical reduction destruction efficiency was not, however, found to depend on the nature of the anion. The studies thus confirmed the possibility of changing the efficiency constant of electrochemical reduction destruction by changing the composition of the electrolyte solution. Figures 5, table 1; references 13: 10 Russian, 3 Western.

**The Structure of the Adiabatic Surface of the Potential Energy of the Ground Electron of an Ozone Molecule**

927M0156A Novosibirsk *ZHURNAL STRUKTURNOY KHIMII* in Russian Vol 32 No 6, Nov-Dec 91 (manuscript received 9 Mar 89) pp 15-20

[Article by R.M. Minyayev, Physical and Organic Chemistry Institute, Rostov State University; UDC 547.173+539.194]

[Abstract] The author of this article examined the structure of the surface potential energy of  $O_3$ . He did so by plotting its gradient field as calculated by the MINDO/3 (modified intermediate neglect of differential overlap/3) method. During the course of his analysis, he introduced the concept of the "minimum-energy gradient line," which is defined as follows. For any two adjacent minima between which a first-rank saddle point lies, there is one and only one gradient line connecting these minima and passing through the corresponding saddle point. This gradient line is the "minimum-energy gradient line." The minimum energy gradient line for surface potential energy goes to infinity on both sides of the given minimum or else terminates in a pole, i.e., a point at which the total energy of the molecule goes to infinity. The minimum energy gradient line coincides with the minimum energy reaction path in various segments. The minimum energy gradient line, like other gradient lines, is calculated not in mass-weighted coordinates as the IRC and meta-IRC, but rather in ordinary normal coordinates. The domain structure of the surface potential energy of  $O_3$  is detailed in two diagrams. Figures 2, tables 2; references 28: 4 Russian, 24 Western.

**Sorption Concentration and Atomic Emission Determination of Selected Microelements in Fresh Waters**

927M065B Kiev *KHIMIYA I TEKHOLOGIYA VODY* in Russian Vol 14 No 6, Jun 92 (manuscript received 21 Jan 92) pp 418-422

[Article by L.I. Kovalchuk and L.V. Kobeleva, Physical Chemistry Institute imeni A.V. Bogatskiy, Ukraine Academy of Sciences, and Water Transport Hygiene

Scientific Research Institute, Ukraine Ministry of Health, Odessa; UDC 543.423:543.064]

[Abstract] An accelerated atomic emission method of analyzing microcomponents present in drinking water in order to evaluate its quality and degree of pollution was developed. Sulfide ion-modified hydrated tin dioxide was used as a sorbent. The sorbent was modified by treating it in a reagent solution so that a film facilitating microcomponent sorption would form on its surface. A 1% sodium sulfide solution was used as a modifier. The sorption concentration was conducted by the static method: A 100-ml sample of water that had been pre-evaporated from 1 l to 0.1 l was placed in a flask to which 0.1 g sorbent was also added. The mixture was stirred for 2 hours. The transparent liquid layer formed was poured off, and the solution and sediment were transferred to a TsLS-3 centrifuge and centrifuged for 5 minutes at a rate of 1,000 rpm. The liquid was poured off, and the sediment was dried out to a constant mass under an infrared lamp. It was transferred to a quartz crucible and roasted in a muffle furnace at 350-450°C for 30 minutes to remove any organic compounds present in the water. Experiment demonstrated that the optimal conditions for concentration of the modified hydrated tin dioxide are as follows: pH, 8 to 10; volume of solution to mass of sorbent, 1,000; and stirring time, 2 hours. Because slightly salty waters have a pH of 8 to 8.5, the concentration was conducted at the natural acidity of the water sample. The spectral analysis was performed with a DFS-8 spectrograph, a three-lens illumination system, a slit width of 0.015 cm, an alternating-current arc of 10 A, graphite electrodes with a 7.0-mm crater on the bottom and a diameter of 3.8 mm, and an exposure time of 60 seconds. The new method has been demonstrated to be capable of determining traces of Al, Fe, V, Cd, Co, Mn, Cu, Mo, Ni, Pb, Ti, Cr, and Zn in concentrations as low as  $5 \times 10^{-8}$  to  $4 \times 10^{-9}$  in drinking water with a concentration coefficient of  $1 \times 10^4$ . The concentration method used is highly efficient, and the fact that sulfide ion-modified hydrated tin dioxide is used as a sorbent makes it possible to determine a number of elements in drinking water simultaneously. Because the new method does not require many laborious stages to prepare samples for analysis, it results in a significant time and reagent savings. Furthermore, the concentration stage may be implemented under field conditions. Tables 5; references 12 (Russian).

**Quantitative Evaluation of Nitrogen Cycle Processes During Application of Increasing Doses of Nitrogen Fertilizers. Second Communication**

927M0164A Moscow AGROKHIMIYA in Russian No 5, May 92 (manuscript received 5 Dec 91) pp 3-10

[Article by V. M. Semenov, A. A. Mergel, L. N. Rozonova, T. V. Kuznetsova, V. N. Kudeyarov, Institute of Soil Science and Photosynthesis, Russian Academy of Sciences, Pushchino, Moskovskaya Oblast; UDC 631.41:631.811.1:631.445.25:631.84]

[Abstract] The question of a direct and indirect effect of nitrogen fertilizers on the mobility of soil nitrogen and the role of the plants themselves in accumulation of additional nitrogen is debatable to this day. Vegetational experiments were carried out in greenhouses by the method of isolated nutrition (soil was isolated from the nitrogen fertilizers). It was shown that the fertilizer stimulated the growth of plants and intensified their pick-up of the soil based nitrogen. Excessive supply of fertilizer nitrogen led to lower accumulation of the dry mass by corn and to lower levels of the "extra nitrogen" in these plants. The intensity of the absorption of soil nitrogen by the plants was directly proportional to the increase of green mass of the experimental corn and its roots in the soil compartment. Nitrogen fertilization of the plants intensified mineralization of the microbial biomass in the soil. The plants used an additional 50% of mineralized nitrogen of the microbial biomass; the indirect effect of this was manifested by a 4.4-8 fold increase in the soil production of CO<sub>2</sub>. The "extra nitrogen" found in plants was the result of direct action of the additive phase of organic soil substances (40%) and by the effect of the "physiological factor" (60%). The latter was the result of the stimulation by the fertilized plants of the nitrogen cycle in the soil (2/3) and by activation of the absorption function of such plants (1/3). Tables 5; references 8: 7 Russian, 1 Western.

**Effect of Nitrogen Fertilizer on Nitrogen Consumption Dynamics and on Quality of Potato Tubers**

927M0164B Moscow AGROKHIMIYA in Russian No 5, May 92 (manuscript received 11 Jun 90) pp 11-17

[Article by T. Mazur, A. Voytas, Agricultural Technical Academy, Olsztyn, Poland; UDC 631.842.4:631.811.1:633.49]

[Abstract] The goal of this work was to investigate in field studies the effect of increasing levels of nitrogen on its assimilation by potato and on the content of some organic compounds in tubers. The nitrogen was applied in quantities of 0, 40, 80, 120, 160 and 200 kg/hectare as ammoniacal potassium nitrate; the phosphorus and potassium fertilizers were kept uniformly at 52.8 and 149.4 kg/hectare, respectively. Analysis of the average values obtained during 3 years showed that increased level of nitrogen fertilizer resulted in its increase in green tops and in the tubers. The optimal level of the fertilizer

N80 gave a 4.5 tons/hectare increase in the harvest. Higher levels of nitrogen increased the growth of large tubers. Nitrogen fertilization showed a negative effect on the content of starch in potato tubers but produced an increased level of general protein and albumen. Nitrogen fertilization led to a slight increase in some essential and nonessential aminoacids as well as in solanine and citric acid. The total sugar content increased with administration of N<sub>80</sub> of up to 80 kg/hectare. Tables 4; figures 2; references: 7 Western.

**Investigation of Concurrent Application Effect of Phosphorus and Silicon Containing Fertilizers on Phosphate Regime at Principal Kazakhstan Soils. 3 Communication. Effect of Silicon on Sorption Capacity of Colloidal Soil Fractions in Respect to Phosphates**

927M0164C Moscow AGROKHIMIYA in Russian No 5, May 92 (manuscript received 17 Sep 91) pp 25-30

[Article by A. L. Ivanov, Kazakhstan Agricultural Institute, Alma-Ata; UDC 631.811.93:631.414.3:631.416.2(574)]

[Abstract] Experimental results were reported on the study of various colloidal soil fractions of common chernozem and the gray soil in respect to their structural and functional properties and the ability of absorb phosphates. These properties were analyzed as a function of the form of silicon containing fertilizers used on them. The x-ray and thermal analyses did not identify any marked changes in the study material. The 0.1 μ chernozem fraction contained 1.5 fold more water than the 0.1-0.2 μ fraction; the grey soil did not show such a marked difference. On the other hand, the 0.1-0.2 μ colloids contained 1.5-2 fold greater quantities of organic material with aromatic-naphteno- aliphatic structure. Introduction of silicon containing compounds lowered significantly the fixating ability of the phosphates (from 10 to 8 mg-eq PO<sub>4</sub>/100 g of soil) in the 0.1 μ colloidal fraction. Tables 2; figures 2; references: 8 (Russian).

**Effect of Fertilizer Doses on Moisture and Nutrient Content in Common Chernozem and on Productivity of Sunflower**

927M0164D Moscow AGROKHIMIYA in Russian No 5, May 92 (manuscript received 15 Aug 91) pp 57-62

[Article by N. I. Kharchenko, All Union Scientific Research Institute of Corn, Dnepropetrovsk; UDC 631.816.1:631.432.2:631.41:631.811:631.445.4]

[Abstract] Under conditions prevailing in the northern steppe area in Ukraine, the factors limiting the growth and development of sunflower are inadequate content of moisture and nutrients in the soil. The effect of a double dose of mineral fertilizers was evaluated to determine if that could increase the water and the nutrients in the

soil. The field studies were carried out during 1985-1987; the fertilizer was increased to N90P90K90. The soil in the experimental area was the heavily loamy chernozem low in humus. Three hybrids of sunflower (Pochyn, Sanbred 254 and Soldor 220) and two standard local brands (6540 and Kharkovskiy 50) were used. Overall, doubling the fertilizer dose preserved water and the nutrients in the soil. The hybrid plants utilized more economically both the water and the nutrients and the yield of hybrid seeds was greater than that of the local brands by some 2.0 hundred-weights per hectare. Overall yield of the sunflower increased only marginally using N90P90K90 fertilizer. Tables 4.

**Effect of Long Term Fertilizer Application on Fertility of Soddy-Podzolic Soil With Different Methods of Basic Tillage**

927M0164E Moscow AGROKHIMIYA in Russian No 5, May 92 (manuscript received 6 Mar 91) pp 90-95

[Article by A. N. Bakun, N. N. Lyubinetskiy, Chernyiv Experimental Agricultural Station; UDC 631.82:631.445.24:631.452:631.51]

[Abstract] The effect of fertilization on productivity of local cultures and principal agrochemical indices in the soil was investigated at the Chernyiv Oblast experimental agricultural station. It was shown that introduction of 14-17 ton/hectare of N51P37K52, N76P55K78 and N102P74K104 fertilizer on soddy-podzolic soils led to a stable balance of humus in the arable layer and an increased of the labile phosphorus and metabolizable potassium in the soil on which crop rotation was practiced. Surface disc cultivation of the soil for a prolonged time without any changes led to a more intensive humus accumulation in the arable layer than observed with variable depth tilling. Productivity was higher in the latter case. One reason for this may be the fact that

differentiation of the arable layer in respect to the nutrition elements makes them unavailable to the plants during the dry season. Regardless of the system of soil tilling, under conditions of crop rotation practiced in Polesya, the optimal dose of mineral fertilizers was N51P37K52 using a 17 ton per hectare application. In case of grain-tilled crop rotation system the best fertilizer is N76P55K78 applied at a rate of 14 tons per hectare. Tables 3; references: 8 (Russian).

**Dynamics and Balance of Humus in Soils With Different Intensity of Cultivation Under Conditions Prevalent in North Eastern Ukraine**

927M0164F Moscow AGROKHIMIYA in Russian No 5, May 92 (manuscript received 2 Aug 91) pp 96-101

[Article by G. I. Uvarov, A. I. Ivanov, Sumy Agricultural Institute; UDC 631.417.1(477)]

[Abstract] The balance of humus in principal soil types at the brand testing plot and on basic farms was studied. Currently there is an active destruction process underway of the organic material in culture agrophytocenoses at a rate which depends on the local agricultural practices. Overall, the reserves and the actual content of humus has been lowered significantly. Intensive soil utilization at the brand testing plots during the past 20-48 years, even with application of 15 tons per hectare of organic fertilizer on soddy-podzolic soil or 6.6 tons per hectare on chernozem resulted in a negative balance of humus. As an illustration, the content of humus was 8.1% in typical virgin land chernozem, 5.9% in arable land after 52 years of continuous use and 5.4% after 100 years. The reason for this sharp decline of the humus content are low doses of applied organic fertilizers and increased accumulation of weeds along with continuous removal of nutrients with collection of every harvest. Tables 3; references: 11 (Russian).

**Effective Parameters of Static Coupled  
Physicomechanical Fields in Matrix Composites**

927M0141A Kiev FIZIKO-KHIMICHESKAYA  
MEKHANIKA MATERIALOV in Russian Vol 27 No 4,  
Jul-Aug 91 (manuscript received 1 May 91) pp 105-111

[Article by V.A. Buryachenko and V.Z. Parton, Moscow  
Institute of Chemical Machine Building; UDC 539.4]

[Abstract] The development of modern equipment operated under conditions of complex loads resulting from interacting physical factors has stimulated the creation of the theory of coupled fields in elastic bodies in general and in composites in particular. The authors of the study reported herein have developed a variation of the effective field method that may be used to estimate the effective parameters of a broad class of stationary coupled fields in matrix composites. A matrix composite is assumed to be subject to the effects of an arbitrary number of stationary coupled (electromagnetic) fields. The variation of the effective field method developed to calculate the effective parameters of these fields is based on solving the problem of the inclusions' binary interaction in an effective field. The calculations are performed under the assumption that all of the arbitrary fields considered are ergodically and statically uniform. The cases of one and two inclusion in an unrestricted matrix are considered. The analysis presented thus demonstrates that the problem of estimating the effective parameters of composites may, for a broad class of stationary coupled fields, be reduced to an investigation of noncoupled fields. Figures 3; references 21: 11 Russian, 10 Western.

**An Eddy-Current Instrument To Monitor  
Structural Changes That Occur When Products  
Made of Titanium Alloys Are Heat-Treated**

927M0141B Kiev FIZIKO-KHIMICHESKAYA  
MEKHANIKA MATERIALOV in Russian Vol 27 No 4,  
Jul-Aug 91 (manuscript received 12 Feb 90) p 119

[Article by V.N. Uchanin, Physical Mechanics Institute  
imeni G.V. Karpenko, Ukraine Academy of Sciences,  
Lvov; UDC 620.179.14]

[Abstract] The author of this concise report describes a new eddy-current instrument that is intended for use in monitoring the structural changes occurring in products made of titanium alloys when they are subjected to heat treatment. The new instrument, which is described as an eddy-current high-frequency "structuroscope," has been given the name Alfa. It is based on a high-frequency self-excited oscillator converter with an eddy-current converter winding connected to its working circuit. The new instrument indicates the formation of gas-saturated layers in titanium alloys. When no gas-saturated layer is present, the self-excited oscillator generates a stable signal at frequencies ranging from 100 to 400 MHz.

When a gas-saturated layer is detected, a break in the generation occurs that is registered by indicators. The instrument's threshold sensitivity corresponds to a layer 20  $\mu$ m thick. The eddy-current converter winding has a diameter of 0.5 mm. The monitoring results are displayed by an arrow indicator and light-emitting diode mounted on the instrument's front panel and are also indicated by an audio signal that may be heard by connecting a headset to the instrument. The Alfa is powered by an ac system with a voltage of 220 V and a frequency of 50 Hz. A self-contained dc power source (12 V and -12 V) may also be used. The new instrument measures 170 x 90 x 45 mm and weighs less than 0.5 kg. The Alfa features an automatic configuration and zero-adjustment mode and may be operated at the push of a button. The Alfa is currently being used at a number of machine building enterprises to monitor the quality of heat treatment of products made of the titanium alloys VT 3-1, VT06, VT-14, and VT-20. It is also being used to detect microcracks in titanium alloys, assess the wear of aluminized layers on refractory steel products, and detect structural changes in thin surface layers of products made of nonferromagnetic materials. References 4 (Russian).

**The Electrical Properties of Schottky Diodes  
Produced by Electrodeposition of Metals on  
Gallium Phosphide**

927M0145A Tbilisi IZVESTIYA AKADEMII NAUK  
GRUZINSKOY SSR: SERIYA KHIMICHESKAYA  
in Russian Vol 17 No 4, Oct-Dec 91 (manuscript  
received 26 Jul 90) pp 253-258

[Article by M.V. Bakhtadze, T.A. Laperashvili, I.N.  
Saginashvili, and A.N. Mumladze; UDC  
621.382.2:541.1]

[Abstract] The volt-ampere and volt-capacitance characteristics of Schottky diodes produced by electrodeposition of indium, gallium, and  $\text{In}_x\text{Ga}_{1-x}$  alloys onto electrolytically purified gallium phosphite surfaces were examined. The studies performed demonstrated that Schottky diodes with an imperfection coefficient of  $n = 1.05 \pm 0.02$  may be produced by using a single-stage process entailing electrochemical etching of the semiconductor's surface and precipitation of the metal from an electrolyte containing an  $\text{NaOCl}$  etching complex and the metal being precipitated. The studies further established that the height of the Schottky barrier produced by precipitation of metallic  $\text{In}_x\text{Ga}_{1-x}$  alloys turned out to be significantly less than the height of a barrier produced by precipitating either indium or gallium alone. This finding was explained in terms of the defect model of the formation of the potential barrier at the metal-semiconductor interface. Figures 2; references 16: 4 Russian, 12 Western.

**New Optically Active Compounds for Inducing Ferroelectricity in Liquid Crystals**

927M0145B Tbilisi IZVESTIYA AKADEMII NAUK GRUZINSKOY SSR: SERIYA KHIMICHESKAYA in Russian Vol 17 No 4, Oct-Dec 91 (manuscript received 7 Dec 90) pp 302-305

[Article by K.D. Vinokur, K.G. Dzhabaridze, G.S. Chiklaya, L.K. Sharashidze, and Z.M. Elashvili, Cybernetics Institute, Georgian Academy of Sciences; UDC 532.783-541.651]

[Abstract] New ethers of cholesterol, 1-menthol, and tigogenin with an electron-accepting substituent in the side chain were synthesized. Six new compounds were produced in all.  $\alpha$ -Chlorobutyric acid and  $\alpha$ -chlorophenylacetic acid were used to create a transverse dipolar moment in the molecules of the optically active additive. In the ethers of the above compounds a transverse dipolar moment was achieved by chlorine atoms. The six new compounds synthesized were dissolved in *n*-hexyloxysalicylidene-*n*'-*n*-hexylaniline. The two ethers of cholesterol did not induce ferroelectricity. The two mixtures with tigogenin did induce ferroelectricity but had a very low spontaneous polarization ( $P_c < 10^{-10}$  C/cm<sup>2</sup>). Spontaneous resistances of 1.3 to 1.5 nC/cm<sup>2</sup> were found for the newly synthesized ethers of 1-methanol. The slope of the molecule from the normal to the smectic plane was found to equal  $\theta_e = 7.5$  to  $8^\circ$ . Previously published studies have reported that for alkoxysalicylidenes in whose molecules the 1-methyl radical is directly connected with the conjugate system of the molecule,  $P_c = 2.5$  nC/cm<sup>2</sup>, and the slope equals  $\theta_e = 21.5^\circ$ . The results of the studies performed thus established that replacing the  $-\text{COOC}^*_{10}\text{H}_{19}-$  group in salicylidenes by  $-\text{OCO}-\text{CH}_2-\text{O}-\text{C}^*_{10}\text{H}_{19}-$  results in a decrease in the slope to one-third of its starting value and, consequently, in a significant reduction in the lead of the helix. For this reason, these systems are promising despite their unfavorable slope (which causes a loss of contrast) because they are characterized by comparatively low control voltages that are inversely proportional to the size of the lead. Table 1; references 7 (Russian).

**The Effect of Atmospheric Factors and Mechanical Effects on the Formation of Bulk YBCO Ceramic Products**

927M0146A Minsk IZVESTIYA AKADEMII NAUK BELORUSSKOY SSR: SERIYA KHIMICHESKIKH NAUK in Russian No 6, Nov-Dec 91 (manuscript received 9 Jul 91) pp 18-20

[Article by V.S. Komarov, S.N. Bondarenko, A.A. Shevchenok, A.N. Korshunov, and V.Ya. Furs, General and Inorganic Chemistry Institute, BSSR Academy of Sciences, and Byelarus Republic Powder Metallurgy Scientific Production Association; UDC 538.945; 537.312.62]

[Abstract] The complexity of manufacturing large, long products from the superconducting ceramic YBCO is due to a large set of atmospheric and mechanical factors facilitating the degradation of the superconductive phase into individual stages of the manufacturing cycle. A series of electron microscopy, x-ray phase analysis, and infrared spectroscopy studies were conducted in order to gain a better understanding of the effect that atmospheric factors and mechanical effects have on the quality of bulk products produced from YBCO superconducting ceramic. The studies established that the nature of the defects present in the said ceramic products, their formation mechanism, annealing, and their reaction with chemically active gases depend on the conditions (duration, intensity, and temperature) and mechanical actions to which the ceramic is subjected during the manufacturing process. Preliminary sintering at 920°C was, for example, found to exert a significant effect on the nature of the processes occurring in YBCO ceramic. Pulverization was found to cause increased adsorption of H<sub>2</sub>O and CO<sub>2</sub> from the atmosphere. Additional research demonstrated that this increase in adsorption is related not primarily to an increase in the amount of surface that makes contact with the atmosphere (pulverization results in a doubling of the surface area) but instead with additional adsorption of chemically active gases (water vapors in particular) on flaws. This increase in the amount of flaws present in material that has been pulverized was confirmed by EPR spectroscopy studies. The studies performed also revealed that depending on the intensity and method of application of mechanical forces, the formation of flaws may be associated with a redistribution of oxygen in the bulk of compact material and with a change (decrease) in the average degree of oxidation of copper. This results in the formation of a field of mechanical stresses within the bulk of the ceramic. Processes leading to the elimination of oxygen from the material, local redistribution of ceramic-forming elements (primarily copper), and formation of new non-superconducting phases that are apparent in EPR spectra are intensified in this mechanical-stress field during subsequent heat treatment. The presence of stressed states in the bulk of a superconductive material was also found to intensify the processes of the breakdown of bulk superconductivity that occur under the effect of chemically active atmospheric impurities. An intensification of all types of degradation (with and without the participation of external factors) was observed in zones of elevated mechanical stress. Figures 3; references 4: 3 Russian, 1 Western.

**Organic Dyes for Optical ROM Disks**

927M0149A Moscow KOLLOIDNYY ZHURNAL in Russian Vol 61 No 1, Jan 91 pp 102-123

[Article by T.N. Gerasimova and V.V. Shelkovnikov, Novosibirsk Organic Chemistry Institute, Siberian Department, Russian Academy of Sciences; UDC 667.28:773.79]

[Abstract] Literature data on the use of organic dyes in the optical read-only memory [ROM] disks that are used in recording information by means of semiconductor laser radiation at a wavelength of 780 to 830  $\mu\text{m}$  was summarized and systematized. The authors concentrate on organic dyes for disks of the DRAW type versus the WORM or reversible type. They divide their review into two main sections. The first focuses on recording layers for organic compound-based optical disks, and the second focuses on dyes for optical disks with absorption in the near-infrared range of the spectrum. The following are among the major findings presented. Telluride and its alloys have proved to be the best organic recording media for the following reasons: they have a high resistance to the effects of the oxygen in air and moisture; they are less toxic than other prospective recording materials; they have a relatively low melting point that gives them a high sensitivity; they have a low heat conduction that makes it possible to achieve high recording densities; they may be manufactured comparatively inexpensively; and their optical and thermomechanical properties may be altered by modification of the organic dye applied to them. Several types of organic dyes have been researched from the standpoint of their effectiveness for use with optical disks used in the near-infrared range of the spectrum, i.e., polymethine dyes, dyes of the di(tri)arylmethane and triarylamine series, quinone and quinoimine derivatives, and phthalocyanines and other metal-complex dyes. Thanks to the availability of experimental methods of studying the electron structure of individual dyes and thanks to the development of related quantum chemistry computational formulas, researchers have been able to synthesize organic dyes tailored to use in optical disks used in recording semiconductor laser radiation at the aforesaid wavelengths. Polymethine dyes, metal complexes of phthalocyanines, and dyes of the naphthoquinone series have emerged as the most promising. The growing foreign market for DRAW-type optical disks and announcements pertaining to the development of a flexible carrier for organic dye-based optical recording have and will likely continue to stimulate further research in the area of organic dyes and photothermal materials based on them. Figures 3; references 232: 9 Russian, 223 Western.

#### Reactions of Phosphorus-Containing Compounds With Diazo Compounds and Carbenes

927M0151A Moscow *USPEKHI KHIMII in Russian*  
Vol 61 No 3, Mar 92 pp 564-615

[Article by B.A. Khaskin, O.D. Molodova, and N.A. Torgasheva, All-Union Scientific Research Institute of Chemical Plant Protection Agents; UDC 547.26'118]

[Abstract] The authors of this review have summarized the reactions of different phosphorus-containing systems with diazo compounds and carbenes. They have also discussed the differences between the reactivity of diazo compounds and carbenes. The review is organized into five sections. The first section is an introduction. The second section summarizes published information on

phosphorus-containing acids, salts, ethers, amides, sulfenamides, sulphenyl halides of phosphoric acids, phosphorus halides, and derivatives of one-, two-, and three-coordinated phosphorus atoms in reactions with diazo compounds and carbenes. Specifically, Section 2 deals with the reaction of phosphoric, phosphonic, phosphinic, and phosphorous acids and their esters with diazo compounds; monothio-, monoseleno-, and selenothiophosphoric acids in reactions of alkylation by diazo compounds; salts of monothio- and dithiophosphoric acids in reactions with diazo compounds and dihalogen carbenes; reactions of amides of phosphoric, thiophosphoric, thiophosphonic, and thiophosphinic acids and sulfenamides of phosphoric acid with diazo compounds; and the reaction of phosphorus-containing polysulfides, sulphenyl halides of phosphoric acid, and phosphorus halides with diazo compounds and carbenes. The third section covers phosphines and phosphites in reactions with diazo compounds and carbenes. The following topics are covered in Section 3: reactions of acyclic trialkyl and triaryl phosphines, tertiary cyclic phosphines, and their oxides with diazo compounds; reactions of trialkyl and triaryl phosphines with carbenes; phosphites in reactions with diazo compounds and carbenes; dialkyl phosphites in reactions with diazo compounds; and reactions of dialkyl(thio)phosphites with carbenes. The reactions of diazo compounds and carbenes with phosphorus-containing systems having multiple bonds are the subject of the fourth section. Specifically, Section 4 focuses on reactions of 1,3-dipolar cyclo complexing of diazo compounds and cyclo complexing of carbalkoxy carbenes to phosphorus-containing systems with multiple bonds; phosphorus-containing ylides in reactions with diazo compounds; and reactions of diazo alkanes with ketophosphoryl compounds and phosphoryl isothiocyanates. In the fifth section the authors systematize the behavior of derivatives of one- and two-coordinated phosphorus atoms in reactions with diazo compounds and carbenes. Specifically, the reaction of diazo compounds and carbenes with acyclic derivatives of two- and one-coordinated phosphorus atoms and the reaction of diazo compounds and carbenes with cyclic derivatives of a two-coordinated phosphorus atom are discussed. References 244: Russian, Western.

#### Compounds Containing Phosphorus and Boron

927M0151B Moscow *USPEKHI KHIMII in Russian*  
Vol 61 No 3, Mar 92 pp 616-646

[Article by G.N. Nikonov, A.S. Baluyeva, Organic and Physical Chemistry Institute imeni A.Ye. Arbutov, Kazan; UDC 547.1127'118]

[Abstract] The synthesis and properties of compounds boron-and-phosphorus-containing compounds that include the following fragments: P-B, P-C-B, P-N-B,

P-O-B, P-C-C-B, P-C-C-B, P-C-O-B, P-C-O-B, P-C=C-P, and P-(C)<sub>n</sub> were examined. The existing information on phosphorus-containing borohydrides, carboranes and coordination compounds with phosphorus- and boron-containing ligands were reviewed. The authors' rationale for classifying the compounds examined by the type of fragment sharing phosphorus and boron atoms is related to the fact that phosphorus and boron have different electronic natures and are capable of changing their coordination and forming coordination bonds with metals. They note that when one of the fragments examined is present between the P and B atoms, the effect of the heteroatomic functional groups is akin to an additional reaction whose type and transfer method is determined by a number of factors, including the following: the distance of the heteroatoms from one another, their arrangement in space, and the ability of dividing fragment to "conduct" electron effects. If, for example, the fragment separating the phosphorus- and boron-containing functional groups is a carbon fragment, stabilizing donor-acceptor reactions throughout space will be the most frequent type of reaction observed in compounds with three-coordinated phosphorus and boron atoms, and the result will (most often) be rather stable betaines. Strong donor-acceptor reactions that are transmitted throughout the bond system and that stabilize the resultant compounds are also observed in cases of cyclic compounds containing a C-O polar fragment between heteroatoms. Several examples are presented to illustrate how the introduction of boron-containing functional groups into the molecule of a phosphorus-containing ligand may result in fundamental changes in the metal's coordination sphere. Most of the example coordination compounds containing phosphorylated carborane structures in their ligand were produced in reactions of ligand exchange at the central ions. In a number of cases, the mutual effect of phosphorus- and boron-containing functional groups is shown to not only change their reactivity in conventional organophosphorus or organoboron compound reactions but also to result in a change in the said reactions' directions and in the production of new coordination compounds with unusual bonds and entirely properties. References 139: 33 Russian, 106 Western.

**Mechanism of the Formation of Open H-Associates in Alkyl- and Alkoxybenzoic Acids During Solid Crystal-Liquid Crystal Phase Transitions**

927M0155A Moscow *KHIMICHESKAYA FIZIKA*  
in Russian Vol 11 No 6, Jun 92 pp 806-813

[Article by V.V. Krasnogolovets, G.A. Puchkovskaya, and A.A. Yakubov, Physics Institute, Ukraine Academy of Sciences, Kiev, and Samarkanda State University; UDC 532.783;535.34]

[Abstract] The technique of infrared spectroscopy to investigate the dissociation of cyclic H-bound dimers in crystals of alkyl- and alkoxybenzoic acids close to their melting point was studied. Specimens of the study acids

were prepared for IR spectroscopy study by cooling a melt between carefully polished potassium bromide or polyethylene wafers that were then sealed on the ends with an epoxy resin. The specimens ranged from 10 to 40  $\mu\text{m}$  in thickness. A polarization microscope was used to control their quality and phase-transition temperature. The spectra of solutions of the study acids in  $\text{CCl}_4$  and their gas spectra at temperatures of 470 to 500 K were also measured. Data previously obtained by the authors for n-carbonic and perfluoroalkylbenzoic acids were used for comparison. The study findings were used as the basis for a theoretical model of the formation of polymer open-chain H-bound associates, the presence of which is one of the prerequisites of mesophase formation. According to the model developed, the "melting" of alkyl- and alkoxybenzoic acids occurs in two stages: The transition to a mesophase is preceded by the dissociation of a portion of the cyclic dimers and the formation of stable cybotactic groups, i.e., chain H associates with a somewhat lower H bond enthalpy ( $\Delta H = 31 \pm 1$  kJ/mol). Next, the alkyl radicals "melt" at the transition temperature. The transition to an isotropic liquid is accompanied by further dissociation of the dimers (it is mostly monomers that are formed) and the disordering of rigid nuclei. The interaction occurring between the  $\pi$ -electrons of the benzene rings, which form densely packed "stacks" in a crystalline state, is an important factor in stabilizing the order parameter of the chain H associates, which in turn determines the stability of the H associates themselves. The authors conclude by stating that their proposed mechanism of the restructuring of the H bonds of the study acids in the pretransition range is based on two types of oscillations that are characteristic for the H dimers of benzoic acids, namely,  $\rho(\text{OH})$  and  $\alpha_{\text{perpendicular}}(\text{OH})$  oscillations leading to the repulsion of a proton from the O-O axis and relatively strong low-frequency polar oscillations [ $\gamma(\text{CCC})$  and  $\beta(\text{CCH})$ ] of the benzene ring that also affect the dynamics of the proton in the H bond. Figures 4, tables 2; references 22: 9 Russian, 13 Western.

**Correlation Diagrams and Symmetry Properties of the Adiabatic States of a System of Two Linear Dipole Molecules**

927M0155B Moscow *KHIMICHESKAYA FIZIKA*  
in Russian Vol 11 No 6, Jun 92 pp 814-823

[Article by A.I. Mayergoyz, Ye.Ye. Nikitin, and Yu. Troye, Chemical Physics Institute imeni N.N. Semenov, Russian Academy of Sciences, Moscow, Physical Chemistry Institute, Gottingen University, Germany; UDC 541.14]

[Abstract] The properties of the symmetry of the adiabatic states and correlation diagrams of the energy levels of a system of two linear dipolar molecules were examined. The study, which was conducted within the framework of a joint project supported by the USSR Academy of Sciences and the Deutsche Forschungsgemeinschaft [German Researchers' Society], was undertaken in an effort to develop an overall classification of the states of

adiabatic channels of the decay of a multiatomic complex into two dipolar linear fragments. The researchers examined a system of two linear dipolar rotators A and B with a fixed distance (R) between their mass centers and with a fixed orientation in space. The bounds of the disturbed rotator and the harmonic oscillators were considered, and the factors involved in the degeneration were determined. On the basis of the theoretical examination presented, the researchers concluded that as in the case of a charge-dipole interaction, the correlation diagrams of a dipole-dipole system manifest several regions of interaction, namely, a region of disturbed rotators, a region of two two-dimensional anharmonic oscillators or librators, and a region of two two-dimensional harmonic oscillators. The correlation diagrams constructed during the study indicate that the interaction of states in these regions is rather complex. The authors conclude by stating that the adequacy of the diagrams presented as a description of the actual situation occurring in a system of two linear dipolar molecules can only be determined by numerical calculations of the potential energy in adiabatic channels and that they will present such calculations in another article (also published in the June 1992 issue of *KHIMICHESKAYA FIZIKA*). Figure 1, table 1; references 26: 1 Russian, 25 Western.

#### The Prospects of Applying RYDMR Spectroscopy to Chemical Physics Problems

927M0155E Moscow *KHIMICHESKAYA FIZIKA*  
in Russian Vol 11 No 6, Jun 92 pp 873-878

[Article by S.I. Kubarev, Chemical Physics Institute imeni N.N. Semenova, Russian Academy of Sciences, Moscow; UDC 541.124;538.67]

[Abstract] Since its discovery in 1944, the method of electron paramagnetic resonance [EPR] (electron spin resonance [ESR]) has been used successfully in various areas of chemistry. One important characteristic of ESR (and all analogous methods providing qualitative characteristics for elementary processes) is its sensitivity and time resolution. The sensitivity of ESR is dictated not only by some threshold concentration of paramagnetic particles (about  $10^{12}$  or more spins in a specimen) but also by the recording technique itself. The sensitivity of ESR decreases significantly if the specimen is characterized by either high electric conduction or high dielectric losses. From the standpoint of time resolution, ESR may be used effectively to study study processes with characteristic times greater than the spin-lattice relaxation time. ESR spectroscopy can only establish the role of weak interactions in the kinetics of elementary processes indirectly. The technique of reaction yield-detected magnetic resonance [RYDMR], on the other hand, is much more effective when dealing with these same weak interactions because they are its very essence. While ESR deals with an individual paramagnetic particle that is generated, participates in a reaction, and "dies" as a result of recombination, RYDMR spectroscopy directly follows the trace from the reacting pair of paramagnetic

particles. In other words, RYDMR spectroscopy establishes the prehistory of an elementary chemical act, i.e., it establishes two reacting paramagnetic particles' preparation for recombination. Thanks to optical recording techniques RYDMR spectroscopy is more effective than ESR spectroscopy by a factor of  $10^6$  to  $10^8$ . In view of these facts, RYDMR spectroscopy may be used in solving a variety of problems of chemical physics, including the following: 1) investigation of the role of intermediate short-lived pairs of paramagnetic particles in the kinetics of complex homogeneous and heterogeneous chemical reactions and catalytic processes on a new level; 2) investigation of energy and electron transfer during photoexcitation in donor-acceptor systems and investigation of the mechanisms of natural photosynthesis; and 3) radiolysis of solids and liquids, including investigation of the effect of ultralow doses of ionizing radiation on objects in radiation biology and medicine. These and other possible applications of RYDMR spectroscopy are discussed. Figures 2; references 24: 13 Russian, 11 Western.

#### The Effect of Structural Factors on Spin Density Delocalization in Nitroxyl Radicals of the Imidazoline Series

927M0156B Novosibirsk *ZHURNAL STRUKTURNOY KHIMII* in Russian Vol 32 No 6, Nov-Dec 91  
(manuscript received 11 Oct 90) pp 42-51

[Article by S.A. Malinovskaya, P.V. Schastnev, R.N. Musin, S.A. Mustafayev, and I.A. Grigoryev, Chemical Kinetics and Combustion Institute, Siberian Department, USSR Academy of Sciences, and Organic Chemistry Institute, Siberian Department, USSR Academy of Sciences; UDC 541.67]

[Abstract] The authors of the study reported herein used the techniques of  $^1\text{H}$  and  $^{13}\text{C}$  NMR and ESR to examine the effect of structural factors on spin-density delocalization in nitroxyl radicals of the imidazoline series. Specifically, in order to determine the effects of substituents at the  $\alpha$ -carbon atoms of the radical center, the researchers analyzed a set of known constants of isotropic hyperfine interactions with  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{14}\text{N}$  nuclei in 3-imidazoline and 3-imidazoline-3-oxide nitroxyl radicals with  $\text{OCH}_3$  substituents in positions 2 and 5 of the cycle. They then conducted a quantum-chemical study of the radicals having a methyl group in position 4. A WP-200SY spectrometer (Bruker) was used for the  $^1\text{H}$  and  $^{13}\text{C}$  NMR studies, and a Bruker CXP-300 spectrometer was used for the  $^{14}\text{N}$  NMR studies. The constants of hyperfine reaction and spin-density distributions were calculated by using the method of intermediate neglect of digital overlap [INDO] in an approximation of the unrestricted Hartree-Fock (UHF) method. The studies performed revealed that the effect of the substituents depends on their electronegativity properties. The unusually strong effect of substituents on the constants of hyperfine interaction with nuclei of the fragment  $\text{PhC} = \text{Y}$  ( $\text{Y} = \text{N}$ ,  $\text{N} \rightarrow \text{O}$ ) separated from the N-O radical center by C2 and C5 saturated atoms that

was discovered during the studies was attributed to a change in the nature of the fragment's spin polarization. For 2-substituted radicals, the spin density in the PhC group was positive, while that in the Y group was negative. For 5-substituted radicals, the signs of the densities and constants were just the opposite. The analysis presented demonstrates that this effect increases as the electronegativity of the substituents increases. Figure 1, tables 8; references 8 (Russian).

**The Structure of Crystals of Inorganic Coordination Compounds With  $[MA_nX]$  and  $[MX_nA]$  Complex Ions Containing Neutral (A) and Acidic (X) Ligands From the Standpoint of Very Dense Packing**

927M0156C Novosibirsk ZHURNAL STRUKTURNYOY KHMII in Russian Vol 32 No 6, Nov-Dec 91 (manuscript received 22 Apr 91) pp 137-150

[Article by N.V. Podberezskaya, T.S. Yudanov, S.A. Magarill, Ye.N. Ipatova, G.V. Romanenko, N.V. Perukhina, and S.V. Borisov, Inorganic Chemistry Institute, Siberian Department, USSR Academy of Sciences; UDC 548.0.31.736]

[Abstract] The crystalline structure of more than 40 coordination compounds containing quasi-spherical ions represented by the formulas  $[MA_nX]$  and  $[MX_nA]$  (where A designates a neutral ligand and X designates an acidic ligand) was analyzed. Compounds containing organic ligands were excluded from the study. The analysis performed established that the crystalline structures of the said compounds are all based on a very dense (fluorite or halite) face-centered packing of the complex ions and may thus be described in terms of a single structural diagram. The researchers also traced the successive transitions from cubic to monoclinic symmetry while general packing motifs are maintained. In their concluding remarks, the authors state that compounds of the  $[MA_nX]Y_n$  (where Y is an acidic ligand and  $n = 1, 2, 3$ ) and  $B_n[MX_nA]$  (where  $n = 1, 2, 3$ ) types are strong physical evidence of a class of structures with the symmetry of the rhombic three-dimensional group  $Pnma$ , which was predicted back in 1951 by N.V. Belov. The distinctive feature of this class of compounds is the population of mirror planes by metal atoms and the arrangement of general-position atoms between these planes, which is to say that the reflex with the index (040) should be very intense in roentgenograms. The researchers further noted that changing the central atom of one of the study compounds does not generally change its structural type and that structural manifestation of a *trans*-effect can only be found in a rather long series. A tendency toward shortening of the length of the *trans*-bond is observed, however, when the ligand is replaced by a ligand with greater electronegativity. Replacement of the outer-sphere ion in both types of coordination compounds studied either leaves the compound's structure unchanged or else results in a decrease in symmetry. Alkaline metals and the ammonium ion in

$B_2[MCl_5(H_2O)]$  are among the compounds that maintain their structural type. Figures 4, tables 2; references 86: 30 Russian, 56 Western.

**Photodesorption Processes During a Semiconductor-Metal Phase Transition**

927M0159A St. Petersburg VESTNIK SANKT-PETERBURGSKOGO UNIVERSITETA in Russian Series 4 No 2, May 92 (manuscript received 6 Jun 91) pp 17-21

[Article by N.L. Levshin and S.Yu. Poroykov; UDC 536.631]

[Abstract] In an effort to gain a better understanding of the photodesorption processes occurring during a metal-semiconductor phase transition, the authors of the study reported herein examined polycrystalline  $VO_2$  films (about 0.3  $\mu m$  thick) on sapphire substrates. An MKH-7301 monopole mass spectrometer was used as a gas-phase analyzer to study the desorption characteristics of the  $VO_2$ . The measurements were taken in a vacuum at a pressure of about  $10^{-6}$  Pa. The thermodesorption spectra of the specimens were recorded while the specimen was in a quartz cell that had been preheated to 700 K. The thermodesorption was conducted in a graduated heating mode (with 30 minutes of thermal stabilization at each point). An IKS-25 photoflash lamp with a pulse duration of 1 ms and energy density of 0.5 J-cm<sup>-2</sup> was used in studying the photodesorption of atoms and molecules from the specimens' surfaces. The effect that flaws induced by ultraviolet irradiation of a specimen's surface have on the dependence  $R(T)$  ( $R$  being the specimen's resistance) were also studied. The studies performed established that in the comparatively narrow temperature interval from 300 to 350 K, the metal-semiconductor phase transition results in a significant change in both thermo- and photodesorption. Both the contribution of thermodesorption ( $Y^T$ ) and that of phase transition ( $Y^{Ph}$ ) were observed to increase sharply as the study films effected the transition from semiconductor to metal. Ultraviolet irradiation of the study  $VO_2$  films was found to be accompanied by a change in electrophysical parameters. The changes that occurred were not completely reversed after the films were removed to the open air. The UV irradiation-induced flaws in the study films were most clearly apparent in the metal phase. This finding was found to be consistent with the increase in the amplitudes of atoms' oscillation in the metal phase. The specific results of the experiment measuring the effect of UV irradiation on the dependence  $R(T)$  were as follows:  $R(T)$  remains unchanged at doses of about  $5 \times 10^{20}$  (photons  $\times cm^{-2}$ ) or less. As the dose was increased to  $5 \times 10^{21}$  (photons  $\times cm^{-2}$ ), the resistance of the specimen in a phase transition gradually decreased; however, no significant changes in hysteresis width or phase transition temperature were observed. When the UV irradiation dose was increased to  $8 \times 10^{22}$  (photons  $\times cm^{-2}$ ),  $R$  decreased approximately by a factor of 60 (in the low-temperature phase), the phase transition was

blurred, the phase transition temperature decreased ( $\Delta T_c$  being about 1 K), and the width of temperature hysteresis increased by 1 K. The expansion of the temperature hysteresis loop and decrease in  $T_c$  were attributed mainly to a decrease in critical temperature when the specimens were cooled. References 11 (Russian).

**The Molecular and Crystalline Structure of Pentamethylferrocene ( $\eta^5\text{-C}_5\text{H}_5$ )Fe( $\eta^5\text{-C}_5\text{Me}_5$ ) in the Interval From 153 to 293 K. Analysis of Thermal Motion in the Crystal Based on X-Ray Diffraction Data**

927M0160B Moscow METALLOORGANICHESKAYA KHIMIYA in Russian Vol 5 No 3, May-Jun 92 (manuscript received 3 Apr 91) pp 579-589

[Article by I.Ye. Zanin, M.Yu. Antipin, Yu.T. Struchkov, A.R. Kudinov, and M.I. Rybinskaya, Elementoorganic Compounds Institute imeni A.N. Nesmeyanov, Russian Academy of Sciences, Moscow; UDC 548.737]

[Abstract] The authors of the study reported herein conducted an x-ray crystallographic analysis of the crystal pentamethylferrocene ( $\eta^5\text{-C}_5\text{H}_5$ )Fe( $\eta^5\text{-C}_5\text{Me}_5$ ). The study crystals were grown from a solution in methanol and were subjected to x-ray crystallographic studies on a Syntex P2<sub>1</sub> diffractometer at temperatures of 153 and 223 K and on a Khilger and Watts diffractometer at 293 K. The study crystals were triclinic, and their limiting boundary of P1 ( $Z = 2$ ) was preserved throughout the entire temperature range studied. The parameters of the elementary cell at 293 and 153 K were as follows:  $a = 7.819(1)$  and  $7.720(1)$  angstroms,  $b = 8.169(1)$  and  $8.153(1)$  angstroms,  $c = 12.239(1)$  and  $12.143(1)$  angstroms,  $\alpha = 73.14(1)$  and  $72.27(1)^\circ$ ,  $\beta = 85.27(1)$  and  $84.67(1)^\circ$ ,  $\gamma = 62.19(1)$  and  $61.95(1)^\circ$ , and  $V = 660.5(1)$  and  $639.0(1)$  cubic angstroms. The Cp- and Cp<sup>+</sup>-ligands were found to be parallel and to be in an eclipsed conformation. The thermal motion in the crystal was analyzed by using an approximation of the LTS model of a rigid body and a single-parameter model that considered the independent motion of the ligands. The thermal motion analysis was performed by using the THMA-11 program adapted for a PBM PC. The analysis demonstrated that the molecule is not structurally rigid and that it manifests the independent libration motion of one ligand relative to the other. The height of the rotation barriers  $B_s$  as calculated from the ligands' mean-square libration amplitudes ( $\phi^2$ ) are actually identical for both cycles and range from 11(2) to 7.7(6) kJ/mol as the temperature increases from 153 to 293 K. Figures 3, tables 5; references 20: 5 Russian, 15 Western.

**The Crystalline and Molecular Structure of the Hexacoordinate Si Derivative *bis*(Benzo-N,N-Dimethylhydrazonato-O,N)-Chloro(Methyl)Silicon**

927M0160C Moscow METALLOORGANICHESKAYA KHIMIYA in Russian Vol 5 No 3, May-Jun 92 (manuscript received 17 May 91) pp 658-665

[Article by A.O. Mozhukhin, M.Yu. Antipin, Yu.T. Struchkov, B.A. Gostevskiy, I.D. Kalikhman, V.A. Pestunovich, and M.G. Voronkov, Elementoorganic Compounds Institute imeni A.N. Nesmeyanov, Russian Academy of Sciences, Moscow, Irkutsk Organic Chemistry Institute, Siberian Department, Russian Academy of Sciences; UDC 547.245:547.246+548.737]

[Abstract] The authors of the study reported herein conducted an x-ray crystallographic study of *bis*(benzo-N,N-dimethylhydrazonato-O,N)-chloro(methyl)silicon. A Siemens RZ/PC automatic diffractometer (Mo K $\alpha$ -radiation, graphite monochromator,  $\theta/2\theta$ -scanning in the interval  $2\theta = 2$  to  $55^\circ$ ) was used to perform an x-ray diffraction study of white nontransparent crystals of *bis*(benzo-N,N-dimethylhydrazonato-O,N)-chloro(methyl)silicon decomposed in air. The crystals were found to be monoclinic and to be characterized by the following parameter values at  $-120^\circ\text{C}$ :  $a = 17.541(4)$ ,  $b = 14.471(3)$ ,  $c = 8.472(2)$  angstroms,  $\beta = 106.24(3)^\circ$ ,  $V = 2,064.7(8)$  cubic angstroms,  $Z = 4$ , and  $d = 1.303\text{ g/cm}^3$ . The structure was decoded by the direct method in the limiting boundary C2/c and then refined in an anisotropic approximation to 0.0597 based on 1,694 reflections with an absolute value of  $F$  that was greater than  $6\sigma$ . The studies performed established that the Si atom has an octahedral coordination: the Cl atom and Me group, like the O,N-chelate ligands, occupy *cis* positions at the following distances (in angstroms): Si-N(11), 2.036; S-N(12), 2.015; Si-O(1), 1.771; Si-O(2), 1.780; Si-Cl, 2.197; and Si-C(1), 2.089. The characteristic lengthening of the interatomic distances in structures of hexacoordinate silicon were analyzed by using information included in the Cambridge Crystallographic Database. The analysis established the existence of an inverse relationship between the lengthening of the Si-X bonds and an increase in the coordination number and electronegativity of X (where X = F, O, N, Cl, and C) as the coordination number of the Si atom is varied. The Si-N bond in hexacoordinate silicon was found to be the most "labile." The Si-F and Si-O distances were found to undergo the smallest amounts of bond lengthening. Figures 2, tables 6; references 30: 2 Russian, 28 Western.

**The Complexing of Cp<sub>2</sub>LuBr With Benzylamine. Molecular Structure of *bis*(Cyclopentadienyl)*bis*(benzylamino)(bromo)lutetium**

927M0160D Moscow METALLOORGANICHESKAYA KHIMIYA in Russian Vol 5 No 3, May-Jun 92 (manuscript received 20 May 91) pp 673-678

[Article by I.P. Beletskaya, A.Z. Voskoboynikov, N.I. Kirillova, A.I. Gusev, I.N. Parshina, and G.K.-I. Mago-medov, Chemistry and Technology of Elementoorganic

Compounds State Scientific Research Institute, Moscow, and Moscow State University imeni M.V. Lomonosov; UDC 547.256.6]

[Abstract] The complexing of  $\text{Cp}_2\text{LuBr}$  with benzylamine was examined. All of the syntheses and reactions were implemented under conditions of a high vacuum or with the use of specially purified argon. The possibility of the existence of two types of complexes, i.e.,  $\text{Cp}_2\text{LuBr}(\text{NH}_2\text{CH}_2\text{Ph})$  and  $\text{Cp}_2\text{LuBr}(\text{NH}_2\text{CH}_2\text{Ph})_2$ , was demonstrated. A CAD-4 Enraf-Nonium diffractometer ( $\lambda\text{Mo K}_\alpha$ -radiation, graphite monochromator,  $2\theta \leq 52^\circ$ ) was used to perform x-ray diffraction studies of  $\text{Cp}_2\text{LuBr}(\text{NH}_2\text{CH}_2\text{Ph})_2$ . Its crystals were found to be monoclinic and to be characterized by the following parameter values:  $a = 17.234$ ,  $b = 14.934$ , and  $c = 9.168$  angstroms;  $\beta = 108.31^\circ$ ;  $d = 1.79 \text{ g/cm}^3$ ;  $Z = 4$ ; and limiting boundary, C2/c. In the complex located on axis 2, the  $\text{Lu}(3^+)$  atom was found to have a distorted trigonal-bipyramidal coordination. Two cyclopentadienyl and a bromide ligand were found to be present in the equatorial plane, and two benzylamino ligands were found to be present in the axial positions. The following bond lengths were found (angstroms): Cu-C, 2.62; Lu-Br, 2.758; and Lu-N, 2.50. Figures 2, table 1; references 14: 2 Russian, 12 Western.

#### Synthesis and Molecular and Crystalline Structure of (2,3- $\eta$ -1,4-Diphenylbut-2-ene-1,4-dione)undecacarbonyl Triangulotriosmium

927M0160E Moscow METALLOORGANICHESKAYA KHIMIYA in Russian Vol 5 No 3, May-Jun 92 (manuscript received 7 Jun 91) pp 684-689

[Article by L.V. Rybin, Ye.A. Petrovskaya, M.I. Rybinskaya, M.Kh. Dzhaferov, A.S. Batsanov, Yu.T. Struchkov, and N.A. Shteltser, Elementoorganic Compounds Institute imeni A.N. Nesmeyanov, Russian Academy of Sciences, Moscow; UDC 547.259.4: 547.572.6]

[Abstract]  $\text{Os}_3(\text{CO})_{11}(\text{MeCN})$  was reacted with *trans*-1,4-diphenylbut-2-ene-1,4-dione in boiling hexane. The result was the new  $\eta^2$ -olefin osmium complex  $\text{Os}_3(\text{CO})_{11}(\eta^2\text{-PhCOCH=CHCOPh})$  in a yield of more than 80%. A Siemens RZ-PC automatic diffractometer ( $\text{MoK}_\alpha$  radiation, graphite monochromator) was used to conduct an x-ray crystallographic analysis of the new complex at a temperature of about  $20^\circ\text{C}$ . SHELXTL PLUS software was used to perform all the necessary calculations on an IBM PC. The analysis revealed that the  $\text{Os}_3(\text{CO})_{11}(\eta^2\text{-PhCOCH=CHCOPh})$  crystals were monoclinic and characterized by the following parameter values:  $a = 11.421(2)$ ,  $b = 21.008(3)$ , and  $c = 12.314(2)$  angstroms;  $\beta = 108.30(1)^\circ$ ;  $V = 2,805(1)$  cubic angstroms; limiting boundary,  $P2_1/c$ ;  $Z = 4$ ,  $d = 2.64 \text{ g/cm}^3$ ; and  $\mu(\text{MoK}_\alpha) = 136.4 \text{ cm}^{-1}$ . The  $\theta/2\theta$ -scanning method was used to measure the intensity of 5,603 independent reflections with  $2\theta \leq 60^\circ$ , and 5,124 reflections with  $I/g \ 2\sigma$  were used in the calculations without any correction for adsorption. The heavy atom method

was used to decipher the structure. The studies performed established that the new complex may be considered a derivative of  $\text{Os}_3(\text{CO})_{12}$  with the replacement of one CO group by a  $\pi$ -olefin ligand. The  $^{13}\text{C}$  NMR spectrum of the new compound  $\text{Os}_3(\text{CO})_{11}(\eta^2\text{-PhCOCH=CHCOPh})$  was found to give two signals at  $\delta = 34.07$  and  $34.98 \text{ ppm}$  that were shifted to the high field by about 100 ppm as compared with the signals of the starting compound *trans*-1,4-diphenylbut-2-ene-1,4-dione. Figure 1, tables 2; references 11: 1 Russian, 10 Western.

#### Synthesis of Derivatives of 4-Trifluoromethyl-7-oxycoumarin; Structure of 3-Cyano-4-trifluoromethyl-7-acetoxycoumarin

927M0166G Moscow IZVESTIYA AKADEMII NAUK SERIYA KHIMICHESKAYA in Russian No 6, Jun 92 (manuscript received 8 May 91) pp 1371-1375

[Article by Ya. V. Voznyy, M. O. Dekaprilevich, D. S. Yufit, and Yu. T. Struchkov, Organic Chemistry Institute imeni N. D. Zelinskiy, Moscow; Element Organic Compounds Institute imeni A. N. Nesmeyanov, Moscow; Biochemistry Institute, Yerevan; UDC 548.737:542.253: 547.565.2:547.491:547.814]

[Abstract] Derivatives of 7-oxycoumarin comprise an important group of laser dyes which effectively generate radiation in the 400-500 nm range. They are also used in biology, medicine, and biochemistry as fluorescent materials. With their aid, sensitive detection of the activity of enzymes capable of splitting the glycoside or ester bond becomes possible. Newer fluorescent derivatives of 7-oxycoumarin make it possible to prepare a number of fluorogenic substrates having interesting properties. Previously, during the course of synthesis of 4-trifluoromethyl-7-oxycoumarin, a new fluorescent compound was obtained in low yield. On the basis of mass spectroscopic data it was tentatively assigned the structure 3-cyano-4-trifluoromethyl-7-oxycoumarin. In the present work, the structure of this compound was further confirmed with X-ray structural analysis of its acetoxy derivative. References 11: 3 Russian, 8 Western.

#### Crystalline and Molecular Structure of 1,1'-Divinyl-2,2'-biimidazolyl

927M0166H Moscow IZVESTIYA AKADEMII NAUK SERIYA KHIMICHESKAYA in Russian No 6, Jun 92 (manuscript received 6 Jun 91) pp 1376-1380

[Article by V. I. Sokol, L. V. Baykalova, Ye. S. Domnina, and M. A. Poray-Koshits, General and Inorganic Chemistry Institute imeni N. S. Kurnakov, Moscow; Organic Chemistry Institute, Irkutsk; UDC 547.785.1: 946.47.022]

[Abstract] The non-substituted 2,2'-biimidazolyl molecule is known to have a near co-planar *trans*-structure with an angle of  $4.6^\circ$  between the imidazole rings at the

pitch along the C<sup>2</sup>-C<sup>2'</sup> bond. In the present work X-ray analysis was used to determine the crystalline and molecular structure of the title compound. It was demonstrated that the molecule has a crystallographic symmetry of 2 and a cisoid conformation with a pitch angle of 128° between the imidazole rings. The length of the C<sup>2</sup>-C<sup>2'</sup> bond is 1.485 anstroms compared with 1.423 anstroms for the non-substituted 2,2'-biimidazolyl. Other structural data are also presented. References 6: 4 Russian, 2 Western.

**Some Features of the Crystal and Molecular Structure of N-(1,2,4-Triazole-5-yl)benzamidinium and Its Hydroxide**

927M01661 Moscow IZVESTIYA AKADEMII NAUK SERIYA KHIMICHESKAYA in Russian No 6, Jun 92 (manuscript received 3 Jun 91) pp 1380-1386

[Article by M. G. Kurella, L. G. Vorontsova, A. R. Amamchyan, and V. A. Dorokhov, Organic Chemistry Institute imeni N. D. Zelinskiy, Moscow; UDC 548.73.542.91:547.79]

[Abstract] Heterylamidines are interesting as reagents for heterocyclic synthesis and as chelating ligands. Recently, a method was proposed for the synthesis of the title compound (TA) from 5-amino-1,2,4-triazole, nitriles, and tributylborane. The present work is a continuation of a series of works on studying the structure of

compounds containing the amidine group. X-ray analysis was used to establish the crystal and molecular structure of TA and its hydroxide. Structural data on both compounds are presented. Figures 2; references 11 Russian, 4 Western.

**Crystal and Molecular Structure of 7-Phenyl-1,2,4-triazole-[1,5-a]-1,3,5-triazine**

927M0166J Moscow IZVESTIYA AKADEMII NAUK SERIYA KHIMICHESKAYA in Russian No 6, Jun 92 (manuscript received 26 Jun 91) pp 1386-1389

[Article by M. G. Kurella, L. G. Vorontsova, A. R. Amamchyan, and V. A. Dorokhov, Organic Chemistry Institute imeni N. D. Zelinskiy, Moscow; UDC 547.887.2:792.9,548.737]

[Abstract] The recently prepared compound N-(1,2,4-triazole-5-yl)benzamidinium may be used as a chelating ligand or as a reagent in heterocyclic synthesis to fuse the triazine ring to the triazole ring. The above compound also reacts with ortho-formate ester to form a bi-cyclic compound having two theoretically possible structures. In the present work X-ray analysis was used to determine the structure of 7-phenyl-1,2,4-triazole-[1,5-a]-1,3,5-triazine. It was demonstrated that in cyclization reactions of N-(1,2,4-triazole-5-yl)amidines with electrophilic reagents, the amine nitrogen atom in the triazole ring acts as the nucleophilic site. References 9: 6 Russian, 3 Western.

**Liquid-Phase Chemiluminescence of Organometallic Compounds. Classification of Light Reactions**

927M0160A Moscow METALLOORGANICHESKAYA KHIMIYA in Russian Vol 5 No 3, May-Jun 92 (manuscript received 8 Apr 91) pp 487-498

[Article by R.G. Bulgakov, V.P. Kazakov, and G.A. Tolstikov, Chemistry Institute, Bashkir Scientific Center, Ural Department, Russian Academy of Sciences, Ufa; UDC 535.379:547.1'13]

[Abstract] The work being done at the Chemistry Institute of the Bashkir Scientific Center of the Ural Department of the Russian Academy of Sciences in Ufa in the area of researching the general patterns and classification of chemiluminescent reactions of organometallic compounds was summarized. In the area of the chemiluminescence of alkyl derivatives and metal hydrides with  $O_2$ , researchers at the institute have confirmed their previously proposed mechanism of the generation of electron-excited states of an emitter and luminescence in the disproportionation of peroxy radicals. They have also demonstrated that oxygen is not the sole organometallic compound oxidizing agent that reacts with the formation of  $R = O(T_1)$ : The oxidation of 9-borabicyclo[3.3.1]nonane with  $H_2CrO_4$  yields a triplet-excited cyclooctanone. In the area of the chemiluminescence of metal alkyls during the oxidation of  $XeF_2$ , researchers at the chemistry institute in Ufa have found clear luminescence during the oxidation of metal alkyls and a number of other organometallic compounds by xenon difluoride. The chemiluminescence of metal

cyclopentadienides in a reaction with  $O_2$ ,  $H_2O$ , and  $XeF_2$  is another area where researchers at the chemistry institute in Ufa have done a great deal of work. Researchers at the institute have established the presence of organometallic peroxides based on the appearance of chemiluminescence when water is added to the reaction solutions involved in the auto-oxidation of U (IV) and Cr (II) cyclopentadienides. The chemiluminescence of transition metal carbonyls in a reaction with  $XeF_2$  has also been studied by researchers at the institute. In the area of the chemiluminescence of ionic organosodium compounds, the researchers have discovered chemiluminescence during the oxidation of organosodium adducts in which the sodium cation is associated with the ion-radical (naphthalene, anthracene, pyrene, diphenylanthracene, benzophenone) of aromatic polycyclic hydrocarbon. Chemical redox-activation of the chemiluminescence of organometallic compounds is another area in which researchers at the chemistry institute in Ufa have been active. Unlike the chemiluminescence activation mechanism proposed by Shuster, the mechanism proposed by the researchers in Ufa is not based on the assumption that chemical redox-activation must be realized in the cell  $[A \cdot ROOR]$  but can instead be realized in the bulk of the solution during the diffusion encounter of the oxidized form of the activator with a suitable reducing agent (donor electron). Researchers at the Chemistry Institute of the Bashkir Scientific Center in Ufa have also worked actively in the areas of classifying liquid-phase chemiluminescent reactions of organometallic compounds and in the low-temperature chemiluminescence of organometallic compounds. Figures 3; references 25: 18 Russian, 7 Western.

**The Effect of Acidity of the Medium on Reaction of Triorganophosphines With Alkyl Halides**

927M0153B St. Petersburg ZHURNAL OBSHCHEY  
KHIMII in Russian Vol 62 (124) No 1, Jan 92  
(manuscript received 5 Nov 90) pp 80-83

[Article by V.A. Chauzov, N.N. Guseva, and L.P. Kostina; UDC 547.241]

[Abstract] It is known that effective electrophilic catalysis is required in the alkylation of low-nucleophile compounds of tricoordinated phosphorus. There have been no systematic studies of the effect of the electrophilic properties of the reaction medium with respect to the related reaction of the alkylation of organophosphines, however. The authors of the study reported herein have examined this problem by way of the example of the reaction of triphenylphosphine with amyl chloride and the reaction of dioctyl phenylphosphine with octyl chloride in a medium of solvents with different acid-base properties (14 different solvents were used in all). Absolute solvents distilled in a nitrogen atmosphere were used in all cases. Varian T-60 and Bruker HX-90 spectrometers were used to record PMR and  $^{31}\text{P}$ - $^1\text{H}$  NMR spectra during the experiments. The experiments performed established that the rates of the reactions of triphenylphosphine with amyl chloride and dioctyl phenylphosphine with octyl chloride are much higher in proton media of medium acidity ( $\text{pK}_a$ , 10 to 13) and that they decrease sharply upon a switch to media with higher or lower acidity. The presence of H-bond acceptors in the reaction medium was shown to slow alkylation of the phosphine significantly. A number of by-products were observed to form when alcohols were used as solvents in the reaction of the alkylation of phenylphosphine. The formation of these by-products was attributed to the closeness of the nucleophilicity of phenylphosphine and ethanol, which dictates the possibility of alternative alkylation of the latter by amyl chloride with the formation of hydrogen chloride facilitating the ethylation of phenylphosphine. Triphenyl-2-oxyethylphosphonium chloride was formed when the

alkylation of phenylphosphine by amyl chloride was attempted in a medium of 2-chloroethanol. Table 1; references 6: 4 Russian, 2 Western.

**Synthesis and Anticholinesterase Properties of O,O-Dialkyl-S-(N-butine-2-piperidinyl)thiophosphates**

927M0157D Tashkent UZBEKSKIY KHIMICHESKIY  
ZHURNAL in Russian No 5, Sep-Oct 91 (manuscript  
received 20 Mar 91) pp 42-45

[Article by D.N. Dilimov, B.N. Babayev, L.I. Kugushova, S.N. Moralev, A.A. Abduvakhobov, Bioorganic Chemistry Institute imeni Academician A.S. Sadykov, Republic of Uzbekistan Academy of Sciences, and Evolutionary Physiology and Biochemistry Institute imeni I.M. Sechenov, USSR Academy of Sciences; UDC 542.91+541.69:547.1.118]

[Abstract] A series of new organophosphorus compounds, namely, O,O-dialkyl-S-(N-butine-2-piperidinyl)thiophosphate were synthesized. Four new compounds were synthesized in accordance with Manich's reaction. Their gross chemical formulas and yields are as follows:  $\text{C}_{13}\text{H}_{24}\text{O}_3\text{PNS}$ , 67.8%;  $\text{C}_{15}\text{H}_{28}\text{O}_3\text{PNS}$ , 65.3%;  $\text{C}_{17}\text{H}_{32}\text{O}_3\text{PNS}$  ( $\text{R} = \text{C}_4\text{H}_9$ ), 66.2%; and  $\text{C}_{17}\text{H}_{32}\text{O}_3\text{PNS}$  ( $\text{R} = i\text{-C}_4\text{H}_9$ ), 64.8%. The O,O-dialkyl-S-(piperidinebutine-2-yl)thiophosphates synthesized turned out to be stronger irreversible cholinesterase inhibitors than O,O-dialkyl-S-propargylthiophosphates. The Ellman method was used to determine the constants of irreversible inhibition of mammal and arthropod cholinesterases by O,O-dialkyl-S-(piperidinebutine-2-yl)thiophosphates. The new compounds proved to be highly effective cholinesterase inhibitors when tested with enzyme sources produced from human erythrocytes; equine blood serum; and homogenates of cholinesterases of the grass aphid, fly, and rat brain. According to studies assessing the enzyme activity of the new compounds, adding piperidine rings to a molecule of O,O-dialkyl-S-propargylthiophosphate helps to increase its constant of irreversible inhibition ( $K_2$ ). Table 1; references 7: 6 Russian, 1 Western.

**Kinetic Description of Radical Polymerization in Monomer Monolayers on a Water-Gas Interface**

927M0140D Moscow VESTNIK MOSKOVSKOGO UNIVERSITETA: KHIMIYA in Russian Vol 33 No 2, Mar-Apr 92 (manuscript received 3 Sep 91) pp 197-200

[Article by V.V. Yegorov and A.A. Klyamkin; UDC 541(64+572)]

[Abstract] The authors have proposed a model and kinetic description of radical polymerization of surfactant monomers in condensed liquid monolayers on a water-gas interface. They developed their model after studying the radical polymerization initiated by unfiltered UV-irradiation in a monolayer of N,N-dimethyl, N-cetylacetyl, methacryloylethyl ammonium bromide at 293 K on Langmuir-Blodgett film balances (Lauda) under a constant surface pressure in an argon atmosphere. 2,2,6,6-Tetramethylpyridine-N-oxyl (Tempo) was used as a strong radical polymerization inhibitor. The chain growth reaction rate constant of the N,N-dimethyl, N-cetylacetyl, methacryloylethyl ammonium bromide in true and micellar solutions at 298 K was determined to be 175 l/(mol x s) and 210 l/(mol x s), respectively. These results were taken as an indication of the fact that the chain growth reaction rate constant of N,N-dimethyl, N-cetylacetyl, methacryloylethyl ammonium bromide as a surfactant monomer remains virtually unchanged upon the transition from a three- to a two-dimensional monomer solution as well as upon a change in the packing density of the molecules in the latter. The authors considered their study results confirmation of the following model of the process of radical polymerization in monomer monolayers on a water-gas interface. Immediately after the beginning of the UV-irradiation, the maximum possible number of active centers (growth radicals) form immediately as a result of activation of the monomer (or, more likely, one of its derivatives) in the form of a continuous layer on the water's surface. Upon further irradiation, the number of active centers diminishes sharply as a result of an intensive break. This should lead to a reduction in the polymerization rate. Other reasons for a decrease in the polymerization rate include a decrease in the amount of monomer and an increase in the amount of polymer in the later as the process unfolds. The latter is capable of causing an expansion of the monolayer as a result of a change in conformation of the polymer chain in it. Simultaneously occurring processes of contraction and expansion of the monolayer may cause an extended period of stationary shrinkage during the irradiation process. Figure 1, tables 3; references 3 (Russian).

**The Effect of a Polymer's Composition on the Structure and Properties of Polyacrylonitrile-Based Membranes**

927M0146B Minsk IZVESTIYA AKADEMII NAUK BELORUSSKOY SSR: SERIYA KHIMICHESKIKH NAUK in Russian No 6, Nov-Dec 91 (manuscript received 29 Dec 90) pp 94-97

[Article by A.V. Vildyukevich, V.I. Sokolova, and E.G. Ostrovskiy, Physical and Organic Chemistry Institute, BSSR Academy of Sciences; UDC 678.025.4:539]

[Abstract] Polyacrylonitrile [PAN]-based ultrafiltration membranes are currently produced by a number of Western firms, and work to create PAN-based membranes is under way in a number of formerly Communist countries. Research on PAN-based membranes was conducted in the 1970's; however, there have been no domestic publications on the topic in recent years. The authors of the study reported herein examined the effect of chemical composition on the structure and properties of a homogeneous acrylonitrile polymer and copolymers of acrylonitrile with itaconic acid (in a 98:2 ratio); acrylonitrile, methyl methacrylate, and sodium allyl sulfonate (in a 91:8:1 ratio); and acrylonitrile, vinyl chloride, and sodium styrenesulfonate (in a 47.5:51.0:1.5 ratio). The membranes were formed by using slotted spinnerets with a fixed gap to apply a thin layer of solution onto a polished surface followed by deposition in water. The formed films were rinsed with water to remove the residual solvent. The filtration characteristics of the study membranes were determined on an FMO2-200 membrane filter at a pressure of 0.1 MPa and a temperature of 25°C. An REM-100U scanning electron microscope was used to study the films' structures. The electron microscopy and membrane filter studies performed established that changing the chemical nature of the membrane-forming polymer results in significant changes in the structure of the films produced from solutions of equal concentration. The homogeneous acrylonitrile polymer resulted in a highly porous, friable film structure, whereas the polymer containing an additional 2% itaconic acid resulted in a rather dense sponge. The copolymer of acrylonitrile with vinyl chloride and sodium styrenesulfonate, on the other hand, resulted in the asymmetric structure with a fine surface layer on a large-pore base containing numerous finger-shaped pores oriented perpendicular to the membrane surface that is typical of ultrafiltration membranes. These differences in morphology were linked to differences in the structures and physicomaterial properties of the solutions used to form the films. The differences noted were due to differences in such things as the forming solutions' viscosity, surface stress, and affinity to the membrane-forming polymer's precipitating agent. The studies examining the viscosity of the casting solutions and transport membrane characteristics demonstrated that it is best to use a copolymer of acrylonitrile with itaconic acid when preparing binary polymer/solvent-based membranes. When copolymers of acrylonitrile with vinyl chloride and sodium styrenesulfonate are to be used as ultrafiltration membranes, extra sponging agents must be added to the casting solution. Figures 3, table 1; references 7: 4 Russian, 3 Western.

**New Research Trends in the Field of Ionic Polymerization**

927M0149B Moscow KOLLOIDNYY ZHURNAL in Russian Vol 61 No 1, Jan 91 pp 139-160

[Article by B.L. Yerusalimskiy, High Molecular Compounds Institute, USSR Academy of Sciences, Petersburg; UDC 541.64:542.952]

[Abstract] The set of agents capable of initiating processes of ionic polymerization of various monomers has expanded greatly in the past decade. Many of these agents are being used to solve such practically important problems as producing new polymers, simplifying the conditions under which narrowly dispersed macromolecules are produced, and developing high-yield polymerization processes. The original initiating systems that have been discovered have had a great impact on thinking regarding the mechanism by which macromolecules form in ionic-type processes. The authors of this review have concentrated on this topic because of a lack of comprehensive treatment of the topic in the scientific literature of the former Soviet Union. They have organized their review in three sections. The first deals with cationic processes; specifically, it covers the mechanisms of cationic processes and the mechanism of cationic polymerization of oxygen-containing heterocycles. Specifically, the author notes that the appearance of new cationic initiators drastically altered the old prevailing view that anionic polymerization techniques are superior to cationic techniques because diverse block and multiblock copolymers with a broadly controllable set of physicomechanical properties could be synthesized in anionic systems but not in cationic systems. The replacement of cumyl chloride as a component of initiating systems by ethers of the cumyl series made it possible to achieve living polymer chains instead of quasi-living chains. Qualitatively analogous effects were achieved lately by using the technique of supplementing binary systems of the Lewis acid-tert-alkylchloride type by a catalytic quantity of strong electron donor. Another important development related to cationic processes was the use of various iodine-containing initiating systems for the polymerization of vinyl ethers with polar substituents. Several have been used to synthesize block ligomers with a specified sequence of single-link fragments corresponding to different monomers. More recently, the same initiating system has been used to produce block copolymers containing alkoxy styrene derivatives. The mechanism of polymerization through activated monomers, which is another name for cationic polymerization of oxygen-containing heterocycles, has been used in the synthesis of block copolymers. The second section, which is devoted to anionic processes, covers porphyrin-based initiating systems (with special emphasis on the polymerization of heterocycles and polymerization of polar unsaturated monomers) and polymerization with group transfer. One important advantage of polymerization with group transfer of the same monomers under the effect of conventional anionic initiators (organometallic compounds) is that the process of the growth of living chains is not complicated by side reactions even at room temperature. The final section is devoted to olefin polymerization processes initiated by homogeneous Ziegler-Natta catalysts. Research on the said catalysts in the former Soviet Union is said to have been given a "second wind" in the 1980's thanks to the creation of catalytic complexes with activity levels far surpassing that of heterogeneous systems of the same types. The research conducted disproved the idea of the necessity of

using insoluble Ziegler-Natta complexes to achieve stereospecific polymerization of olefins. Tables 4; references 76: 7 Russian, 69 Western.

#### Heterocyclic Bifunctional Monomers in Polymer Synthesis

927M0149C Moscow KOLLOIDNYY ZHURNAL  
in Russian Vol 61 No 1, Jan 91 pp 161-194

[Article by R.D. Katsarava and D.P. Kharadze, Molecular Biology and Biological Physics Institute, Georgian Academy of Sciences, Tbilisi; UDC 678.02:66.095.3]

[Abstract] The authors of this review have concentrated on that type of activated polycondensation known as the "active cycles" method. The essence of the active cycles method lies in the reaction of *bis*- and polyfunctional nucleophiles with monomers containing various heterocycles as electrophilic functional groups. Three-, four-, five-, and six-membered heterocycles are each treated in a separate section of the review. Special attention is paid to *bis*-epoxides, derivatives, aziridines, *bis*- $\gamma$ -lactones, cyclic *bis*-carbonates, saturated and unsaturated *bis*-azlactones, cyclic *bis*-isomers and *bis*-imides, cyclic *bis*-amides, cyclic *bis*-imino esters and their analogues, *bis*- $\delta$ -lactones, and *bis*-benzoxazinones. Polyadditive-type reactions that entail the opening of the heterocycle and that by and large conform to linear polycondensation laws are examined. A number of the reactions covered, for example, those involving saturated *bis*-azlactones, *bis*-isoimides, *bis*-imides, and selected unsaturated *bis*-azlactones may be classified as polyadditive processes in their "pure" form. In other cases, the reactions "depart" from the "pure" polycondensation process because of hydroxyl, ketone, and other groupings that may be considered "low-molecular by-products"; however, the said reactions do not "abandon" the macromolecular chains and remain covalently bound to them. Such reactions are demonstrated to be promising for use in synthesizing functional polymers that are often inaccessible when conventional polycondensation methods are used. Tables 2; references 139: 54 Russian, 85 Western.

#### The Effect of Carborane Groupings and the Structure of the Surrounding Organic Fragments Surrounding Them on Monomers' Reactivity and Polymers' Properties

927M0151C Moscow USPEKHI KHIMII in Russian  
Vol 61 No 3, Mar 92 pp 647-667

[Article by N.I. Bekasova and N.G. Komarova, Elementoorganic Compounds Institute imeni N.A. Nesmeyanov, Russian Academy of Sciences, Moscow; UDC 678.86:546.27]

[Abstract] Available theoretical and experimental information on research in the area of the effect that carborane groupings and the structure of the organic fragments surrounding them have on the reactivity of their monomers and the properties of their polymers was

systematized. The review is organized into an introduction and three sections focusing on the following topics: the effect of carborane groupings on monomer reactivity, the effect of carborane groupings on the properties of carborane-containing polymers, and the effect that the arrangement of carborane groupings in a macromolecule and the structure of fragments directly connected to them have on the properties of carborane-containing polymers. The problems that the presence of bulky carborane groupings cause in the synthesis of carborane-containing polymers are discussed along with such strategies for solving them as the introduction of various fragments between the amino group and m-carborane nucleus, high-temperature (220°C) polycondensation of a solution of chlorinated biphenyl or acceptor-catalyst polycondensation in an acetone solution, radical copolymerization, and migration copolymerization. m- and n-Carborane isomers are shown to have a greater tendency toward polymer formation than an o-isomer inasmuch as steric problems are less likely to be encountered when the former are used. The importance of the effect of the isomerism of the carborane nucleus on macromolecules' molecular mobility is also demonstrated. The isomerism of a carborane nucleus is shown to have a significant effect on the stability of polyamides, and carborane isomerism is also shown to be important in the process of polyheterocycle formation. Examples are presented that illustrate that although it is generally the case that a polymer's properties depend on which carborane isomer it contains, cases may also be found where carborane isomerism is barely reflected in a polymer's properties. The properties of carborane-containing polymers are shown to be dependent on the location of carborane groupings in the side or main chain of their macromolecules, as well as on the structure of the fragments located alongside the carborane groupings. The properties of carborane-containing polyesters are demonstrated to be especially dependent on the chemical structure of the organic fragments located between carborane groupings, and the heat stability of m-carborane-containing polyamides is shown to be largely dependent on the manner in which the NH-CO bond is attached to the carborane grouping. References 109: 78 Russian, 31 Western.

#### **The Sorption of Vapors by Swelling Polymers. Communication 2. The Sorption of Water Vapors**

927M0157B Tashkent UZBEKSKIY KHIMICHESKIY  
ZHURNAL in Russian No 5, Sep-Oct 91 (manuscript  
received 20 Jun 90) pp 13-15

[Article by Sh.A. Azizov, B. Khodzhaev, S.F. Greben-  
nikov, and M.A. Magrupov, Tashkent Red Labor Banner  
Order State University imeni V.I. Lenin; UDC  
541.64:532.132.677]

[Abstract] In a continuing series of research reports, the  
authors examined the sorption of water vapors by  
swelling polymers. Specifically, they compared the cal-  
culated values of sorption in amorphous ranges and

experimental data for selected commercial and ion-  
exchange fibers, i.e., cotton, polyvinyl alcohol-T [not  
further identified], kapron [a synthetic fiber similar to  
nylon], Anid [the Soviet equivalent of nylon], and  
nitron. Others have proposed that sorption in the amor-  
phous regions of a polymer be calculated on the basis of  
the group contributions of the most characteristic  
polymer groupings. In view of this fact, the researchers  
calculated the above polymers' sorption in amorphous  
regions of polymers by using an isothermal curve equa-  
tion for amorphous-crystal polymers and an expression  
for limiting sorption in amorphous regions. The calcu-  
lated values were found to be in good agreement with  
experimentally obtained values. Next, they calculated  
the characteristic sorption energy of cotton, polyvinyl  
alcohol-T, kapron, Anid, lavsan [a synthetic fiber similar  
to dacron], viscose fiber, and acetate fiber. They derived  
an expression for calculating the ratio of the integral  
sorption heat to limiting sorption ( $q_i/a_0$ ) that may be  
used to estimate the characteristic sorption energy of a  
fiber. Calculations made with the expression established  
an average value of 274 J/g for  $q_i/a_0$  (with an average  
deviation of 19.5%). The characteristic sorption energies  
of the fibers studied were determined to be as follows:  
viscose fiber, 2.00; kapron, 1.38; Anid, 1.66; lavsan,  
1.47; acetate fiber, 1.32; cotton, 2.00; and polyvinyl  
alcohol-T, 1.05. The calculated value of  $q_i/a_0$  for the  
study fibers were as follows: viscose fiber, 5.94 (average  
deviation, 20%); kapron, 3.54 (average deviation, 28%);  
Anid, 4.26 (average deviation, 14%); lavsan, 5.19 (aver-  
age deviation, 5%); acetate fiber, 3.92 (average devia-  
tion, 20%); cotton, 5.28 (average deviation, 7%); and  
polyvinyl alcohol-T, 3.43 (average deviation, 30%). The  
relationships presented were recommended for use in  
predicting the hydrophilic properties of polymer mate-  
rials. References 5 (Russian).

#### **Fluorine-Containing Graft Copolymers of Polyethylene (A Review)**

927M0157C Tashkent UZBEKSKIY KHIMICHESKIY  
ZHURNAL in Russian No 5, Sep-Oct 91 (manuscript  
received 10 Oct 90) pp 27-32

[Article by M.K. Asamov, T.S. Sirlibayev, and I.M.  
Barkalov, Tashkent Red Labor Banner Order State Uni-  
versity imeni V.I. Lenin; UDC 541.64:678(742+743)]

[Abstract] Literature data pertaining to the graft poly-  
merization of polyethylene with fluorine-containing  
compounds was analyzed. The possibilities of using the  
technique of grafting in solving a number of practical  
problems were also assessed. The following are among  
the main conclusions presented. Graft copolymers of  
polyethylene with tetrafluoroethylene are characterized  
by improved heat resistance, heat stability, and chemical  
stability. Postpolymerization may be used in grafting  
tetrafluoroethylene to polyethylene. The technique of  
grafting tetrafluoroethylene onto preirradiated polyeth-  
ylene at room temperature in the absence of a monomer  
has proved to be little effective. The process of using  
sensitizers that reduce the irradiation dose when grafting

polyethylene has been rather well developed. Synergetic systems, i.e., compounds of the acetylene series plus fluoromonomers, have proved to be the most effective sensitizers. The effectiveness of radiation grafting of polyethylene may also be increased by irradiating it in the presence of different mixtures of acetylene and tetrafluoroethylene, butadiene with tetrafluoroethylene, or chlorotrifluoroethylene. Cellular polyethylene irradiated in the presence of an equimolar mixture of tetrafluoroethylene and acetylene at a dose of 4.8 Mrad has retained its shape even at temperatures of 383 K, whereas nonirradiated polyethylene begins to become irreversibly deformed at 351 K. The process of radiation vapor-phase grafting of vinyl fluoride to polyethylene has been shown to occur virtually without the formation of a homopolymer, with the yield of graft copolymer depending on the irradiation dose and dose rate, the nature of the initial condition and structure of the modified polymers, and the presence of gasform additives (oxygen, air, nitrogen). Studies have established that the yield of polyvinylfluoride graft to polyethylene increases in the presence of vapors of methyl and ethyl alcohol, chloroform, and dichloroethane. Studies examining the thermomechanical properties of graft copolymers of polyethylene and polytetrafluoroethylene have confirmed that graft copolymer possesses a higher pour point and thus a higher heat resistance than do starting and irradiated specimens of polyethylene. Studies of the use of recycled polyethylene wastes by low-temperature postradiation grafting of vinyl fluoride have established that graft copolymers of recycled polyethylene with polyvinyl fluoride have improved heat resistance and better mechanical properties than does starting recycled polyethylene. The technique of radiation graft polymerization has been studied; membranes to which more than 25%  $\alpha,\beta$ -tetrafluoroethylenesulfonyl fluoride has been grafted have demonstrated high electrochemical characteristics and thermal properties and may be used as cation-exchange membranes. Surface fluorination of polyethylene has proved to be an important process that makes it possible to use economical materials to produce surfaces with properties close to those of fluoropolymers. Polyethylene treated with an electric discharge has proved to possess a high mechanical strength, chemical resistance, and good compatibility with living tissues. References 31: 6 Russian, 25 Western.

#### **The Properties of Graft Copolymers of Na-KMTs With Polymethacrylic Acid in Aqueous Electrolyte Solutions**

927M0157E Tashkent UZBEKSKIY KHIMICHESKIY ZHURNAL in Russian No 5, Sep-Oct 91 (manuscript received 9 Jan 91) pp 45-48

[Article by F.F. Nuragaliyeva and R.S. Tillayev; UDC 541.64:536.7]

[Abstract] The interaction of a graft copolymer with salts, i.e., sodium chlorides, calcium, and copper was studied. Viscosimetry, potentiometric titration, and turbidimetry studies were performed on specimens of graft

copolymer consisting of Na-KMTs [not further identified] and polymethacrylic acid that was synthesized by radical polymerization of a polymethacrylic acid monomer in an aqueous solution of Na-KMTs in the presence of potassium persulfate at 333 K. The amount of inhibitor used was varied in order to obtain specimens with different amounts of graft polymethacrylic acid. The graft copolymers were identified by the methods of IR spectroscopy and elementary analysis, and the polymethacrylic acid content was determined by titration. The viscosity measurements were taken at 298 K. All of the salts used were graded chemically pure. The studies performed to determine the degree of the cations' effect on conformation of the graft copolymer's macromolecules established that copper chloride has the greatest ability to compress macromolecules. The studies assessing the electrolytes' effect on the turbidimetric titration curves revealed that 'adding copper salts to solutions of the graft copolymer results in an increase in the solutions' optical density when NaCl is added in concentrations from 0.1 to 0.5 and when  $\text{CuCl}_2$  is added in a concentration of 0.01 to 0.05. This effect was attributed to dehydration of the chain as a result of the bonding of the metal ions to the carboxyl groups. The observed loss of solubility was most pronounced when the amount of polymethacrylic acid in the copolymer was elevated. Complexing with metal ions was thus demonstrated to result in changes in the study polymer's properties. Although the copper ion did not form a high-coordination complex with the carboxyl groups of the graft copolymer (i.e., a complex with a coordination number of 4) but instead formed a low-coordination complex (with a coordination number of 2), it nevertheless proved to be an effective "cross-linker" that had a marked effect on the macromolecule's conformation and, consequently, on its acid-base properties. Figures 3; references 7: 6 Russian, 1 Western.

#### **The Polymerization of Methacrylate Ester of Dimethylethynylcarbinol in the Presence of Freon-113**

927M0158C Tashkent UZBEKSKIY KHIMICHESKIY ZHURNAL in Russian No 6, Nov-Dec 91 (manuscript received 20 Feb 91) pp 41-44

[Article by T.S. Sirlibayev, M.K. Asamov, F.Z. Yusupbekova, N.A. Tsagarayeva, and A.L. Ziyayev, Tashkent Labor Red Banner Order State University imeni V.I. Lenin; UDC 66.095.026.678.76]

[Abstract] Polymerization of methacrylate ester of dimethylethynylcarbinol in the presence of freon-113 was examined. Methacrylate ester of dimethylethynylcarbinol was synthesized in accordance with the Favorskii reaction and then acylated by acid chlorides of unsaturated acids of monosubstituted acetylenes. The monomer and the freon-113 used in the experiments were purified by vacuum distillation. Their purity was determined chromatographically. The pure methacrylate ester of dimethylethynylcarbinol was characterized by the following physicochemical constants: molecular

mass, 152; boiling point, 337 K;  $d_{25}^{25} = 0.9537$ ; and  $n_{20}^{20} = 1.4416$ . Dinitryl azobisisobutyric acid was used as an initiator. The reaction was conducted at a temperature of 323 K and a pressure of 0.1 Pa. The resultant polymer was dissolved in dimethylformamide, precipitated by n-heptane, and dried to a constant mass. The polymerization kinetics of methacrylate ester of dimethylethynylcarbinol as a function of monomer:solvent ratio were studied. The said studies indicated that increasing the concentration of freon-113 results in a decrease in the degree of monomer converted. A 1:1 monomer:solvent ratio was determined to be optimal. The studies further established that increasing the concentration of initiator in the presence of freon-113 results in an increase in the maximum degree of monomer conversion (to 98%) and in an increase in the polymerization rate from 0.4 to 1.0%/min. The order of the polymerization reaction with respect to the initiator was found to equal 0.5 and was attributed to the biomolecular breaking of the growing chains. In the temperature interval from 318 to 338 K, the study polymerization reaction was found to obey Arrhenius' law. The total energy of activation in the presence of the solvent was found to equal 18.2 kJ/mol. Viscosity studies established that increasing the reaction temperature from 323 to 333 K reduces the resultant polymer's characteristic viscosity from 1.5 to 0.7 dl/g. Higher temperatures were found to facilitate breakdown of the initiator and the formation of shorter macrochains. Polymer synthesized in the absence of freon-113 was found to have a somewhat higher heat stability than the polymer specimens synthesized in its presence. The polymer specimens synthesized in the presence of freon-113 were found to be more easily processable into products. Figures 3; references 4 (Russian).

#### The Structure of Copolymers of Acrylonitrile and Vinyl Acetate With Selected Fluoroethylenes

927M0158D Tashkent UZBEKSKIY KHIMICHESKIY ZHURNAL in Russian No 6, Nov-Dec 91 (manuscript received 10 Oct 90) pp 53-55

[Article by A.L. Ziyayev, B.Kh. Badyrov, V.L. Maksimov, M.K. Asamov, A.R. Karimov, and T.S. Sirlibayev, Tashkent Red Labor Banner Order State University imeni V.I. Lenin; UDC 547-13:438]

[Abstract] The structure of copolymers of vinyl fluoride with acrylonitrile and tetrafluoroethylene with vinyl acetate was examined. The study copolymers were synthesized in accordance with a method described elsewhere under a pressure of 6 to 10 kgf/cm<sup>2</sup> in a 1.3-liter-capacity stainless steel autoclave equipped with a stirrer and sleeve for heating. The techniques of <sup>1</sup>H and <sup>13</sup>C NMR and x-ray crystallographic analysis were used to study the copolymers' structure. The appearance of a CFH-group doublet in the <sup>1</sup>H spectra of the compound formed when vinyl fluoride was added to polyacrylonitrile molecules was taken as confirmation of the fact that copolymers of vinyl fluoride and acrylonitrile had indeed formed. <sup>13</sup>C NMR spectra were required to

obtain additional information about the resultant copolymers, however. The signals of the <sup>13</sup>C nuclei in the spectra of the study copolymers, which corresponded to CH and CN groups, had a split in the acrylonitrile blocks. The ratio of the intensities of the triplet's components was close to 1:2:1, which indicated that the stereochemical configuration of the acrylonitrile blocks in the copolymer of vinyl fluoride with acrylonitrile is atactic. The introduction of vinyl fluoride links into polyacrylonitrile was found to result in a significant shift of the <sup>13</sup>C signal of the CH<sub>2</sub> groups adjacent to the CFH group with respect to the CH<sub>2</sub> groups of the polyacrylonitrile blocks and to a weaker shift in the <sup>13</sup>C signals of the CH and CN groups. The interaction constant  $I_{C-F}$  for the CH<sub>2</sub> groups was found to amount to 20 Hz for the CH<sub>2</sub> groups and 12 Hz for the CH groups. The signal of the C-groups adjacent to the CFH group was a triplet with an intensity ratio close to 1:2:1. The components of the said triplet were evidently isotactic and syndiotactic triads (-AN-AN-VF-). The ratio of the components' intensities was taken as confirmation of the fact that the segments of alternation of acrylonitrile and vinyl fluoride links in the copolymers' molecules have an atactic stereochemical conformation just as is the case for the polyacrylonitrile blocks. When tetrafluoroethylene was added to polyvinyl acetate molecules, several lines appeared in the NMR spectra instead of the single lines characteristic for the spectra of polyvinyl acetate. The ratio of the molar fractions of different diads and triads, which equaled the ratio of the intensity of the corresponding lines in the spectra, is characteristic of a two-component statistical copolymer whose molecular structure is determined by two copolymerization constants:  $r_{TFE} = 0.19$  and  $r_{VA} = 0.57$ . The x-ray crystallographic studies performed established that the amounts of vinyl fluoride and tetrafluoroethylene links in the copolymers are increased and that the degree of crystallinity of the resultant copolymers also increases. When vinyl fluoride links are present in a copolymer in an amount not exceeding 10% (mass), they are separated by acrylonitrile links and do not form a noticeable amount of blocks. The copolymers synthesized were statistical, and their degree of crystallinity depended on their composition. Figure 1; references 6: 5 Russian, 1 Western.

#### Kinetics of the Accumulation of Paramagnetic Centers in Composite Polymer Films

927M0159B St. Petersburg VESTNIK SANKT-PETERBURGSKOGO UNIVERSITETA in Russian Series 4 No 2, May 92 (manuscript received 6 Jun 91) pp 21-23

[Article by T.A. Mosiyenko and S.P. Pivovarov; UDC 539.28]

[Abstract] Two types of PMF polyimide films that had been subjected to the effect of climate and radiation factors were examined. The study polyimide film specimens were exposed to cosmic rays at the high-mountain station of the High-Energy Physics Institute of the Kazakhstan Academy of Sciences, which stands at an altitude

of 3,340 m above sea level. After this "climatic aging," the films were subjected to  $\gamma$ -irradiation on a unit with a cobalt 60 source. The specimens were irradiated at a dose rate of 75 to 460 rad/s. The climatic aging of the individual study specimens was conducted either in the open air or in a jalousie cabin. The exposure times were varied from 1 to 12 months. The  $\gamma$ -radiation was administered in doses from 1 to 500 Mrad with parallel temperature control. The spectra of the radiation-induced radicals were recorded at room temperature on RE 1301, RE 1306, and ESR-231 electron spin resonance [ESR] spectrometers. Visual observations of the polymer specimens' embrittlement as a result of the irradiation process were also recorded and compared with data from analyses based on examinations made by using an optical microscope. The studies performed established that preliminary exposure to climate factors sharply reduces the radiation resistance of polyimide films. A very low concentration of paramagnetic centers was observed in  $\gamma$ -irradiated film specimens that had not previously been subjected to "climatic aging." In fact, the concentration of paramagnetic centers observed was at the threshold of the spectrometer's sensitivity (less than  $10^{14}$  shifts/g). Length and conditions of preliminary exposure to climate factors both affected the threshold radical concentration and position of the maximum on the active-center accumulation curve. First, the height of the maximum, i.e., the threshold concentration, was found to initially increase as exposure time increased and then to decrease. In other words, the dependence of

$\lg N$  on  $\tau$  is nonlinear and also passes through a maximum. The highest concentration of radicals was on the order of  $10^{19} \text{ g}^{-1}$  and was observed in the dose range from 10 to 100 Mrad. Second, the limiting concentration of radicals was a factor of 1.2 to 1.5 times higher in the case of specimens held in the cabin than in the case of those held in the open air for an equal amount of time. Additional experiments involving irradiation of composite films with and without a transparent coating demonstrated that the relative intensity of the side and central components is also dictated by radiolysis of the transparent coating. The side component proved to be higher for specimens with a transparent coating. At high doses, the accumulation of free radicals was only accompanied by a loss of elastic properties all the way to total embrittlement in the case of those specimens that were subjected to preliminary exposure to the weather. The dependence of embrittlement on radiation dose and exposure time and conditions was so complex that further studies are required. The visual observations revealed that exposed specimens exhibit a loss of transparency. The microscope studies established that the combined effects of climate and radiation result in changes in supermolecular structure, including changes in crystal shape and size and a blurring of the threadlike structures separating crystals' boundaries. Changes in the exposed specimens' mechanical properties were also observed and attributed to the development of internal stresses that were most likely localized along lamellar interfaces. References 5: 3 Russian, 2 Western.

### Magnetic Effects and RYDMR Spectra for Intermediate Short-Lived Radical Pairs Containing Magnetic Nuclei

927M0155C Moscow *KHIMICHESKAYA FIZIKA*  
in Russian Vol 11 No 6, Jun 92 pp 857-866

[Article by Ye.A. Yermakova and S.I. Kubarev, Chemical Physics Institute imeni N.N. Semenova, Russian Academy of Sciences, Moscow; UDC 541.124;538.67]

[Abstract] The dependence of reaction yield-detected magnetic resonance [RYDMR] for a radical pair containing one magnetic nucleus with an arbitrary spin on the parameters of the cell and the radical pair was examined. The theoretical analysis performed was based on an approximation that the researchers describe as rather strict but yet significantly simplified when compared with the general formulation of the problem. Specifically, they used what is termed a secular approximation implemented in a strong constant magnetic field ( $H_0 / g\beta A$ , where  $A$  is the constant of hyperfine interaction). The analysis method used by the authors is said to be a natural continuation of a previous (January 1992) publication by them, which contains a general formulation of the problem of investigation of RYDMR spectra for a cellular model. In the present article the authors attempted to systematize the results obtained from an examination of the appearance of the hyperfine interaction mechanism of spin conversion in RYDMR spectroscopy in pure form. The analysis performed demonstrated that in addition to the inversion of the RYDMR that occurs when the strength of a microwave field is increased, the hyperfine interaction mechanism also results in analogous changes in the spectrum when the recombination rate constant  $H_r$  and the exchange constant  $J$  are varied. The authors also examined the phenomenon of stimulated nuclear polarization and the dependence of the respective spectra on  $H_r$  and  $J$ . This examination was conducted within the framework of the cellular model. The analysis revealed that as in the case of the  $\Delta g$  mechanism of spin conversion, the RYDMR spectra of a radical pair with a magnetic nucleus undergo characteristic changes when the intensity of the microwave magnetic field is varied. Specifically, they manifest the phenomenon of spectrum inversion when the strength of the field is increased. The behavior of the spectrum when other parameters are altered was found to depend significantly on the specified region in which the variation began. The authors concluded by noting that the rather strong effect that a microwave field has on the likelihood of the recombination of radical pairs with identical spins but different hyperfine interaction constants and radical pairs with different spins may turn out to be useful in solving problems of separating spins. Figures 6; references 28: 12 Russian, 16 Western.

### RYDMR Spectra for a Positronium

927M0155D Moscow *KHIMICHESKAYA FIZIKA*  
in Russian Vol 11 No 6, Jun 92 pp 867-872

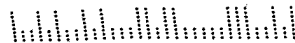
[Article by Ye.A. Yermakova and S.I. Kubarev, Chemical Physics Institute imeni N.N. Semenova, Russian Academy of Sciences, Moscow; UDC 541.124;538.67]

[Abstract] A positronium [Ps] atom represents a metastable system consisting of an electron and positron bound by a Coulomb interaction. It is highly likely that a positronium atom will form in matter when a positron encounters an electron provided that the relative velocity of the two is small (on the order of  $ac = (1/137)c$ , where  $c$  is the speed of light). When this condition is violated, the probability of direct annihilation of the electron and positron upon encounter significantly exceeds the probability of the formation of a bound state. A constant magnetic field has a marked effect on the probability of the decay of a positronium atom. A positronium atom served as the first analogue for the model of a short-lived nonequilibrium pair of paramagnetic particles that was proposed to interpret the effect of a constant magnetic field on electric conduction in organic semiconductors. The positronium is relevant to the field of reaction yield-detected magnetic resonance [RYDMR] spectroscopy for two reasons. First, the calculation of RYDMR spectra for a positronium prompts several new possibilities for implementing magnetic effects in chemical physics. Second, the problem of using a cellular model to calculate the RYDMR spectra of a positronium is directly linked to problems of positronium diagnosis, which has recently become increasingly important as a method of investigating the structure and kinetic properties of such objects as metals and semiconductors, polymers, and superconductors. The authors begin their analysis by demonstrating that from the standpoint of RYDMR spectroscopy, the examination of a positronium is in no way different from the examination of a radical pair that does not contain magnetic nuclei. They proceed to develop theoretical and numerical estimates of RYDMR spectra for a cellular model. According to these estimates, the effect of a microwave field on positronium is by no means small. Both low- and high-frequency RYDMR spectra are affected. According to the curves plotted for the change in the low-frequency RYDMR spectrum of a positronium as a function of  $J$ , for example, the effect of a microwave field amounts to about 4% for resonance ranges, and when  $H_1 = 10$  Oe, it reaches 12%. Similar results are obtained for the change in the high-frequency RYDMR spectra of a positronium as  $H_r$  is varied. Specifically, the effect of a microwave field in resonance changes from 6.5 to 3%, and when  $H_1 = 19$  Oe, the effect varies from 14 to 10%. The numerical estimates made by the authors of this article demonstrate that this sensitivity is rather high and may make it possible to apply a new approach to old problems. Figures 3; references 21: 14 Russian, 7 Western.

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